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Physics

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U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Chemical Physics
Gaithersburg, MD 20899

December 1985



INTRODUCTION

This book is a summary of the technical activities of the NBS Center for Chemical Physics (CCP) for the period October 1, 1984 to September 30, 1985. The Center which is one of four units in the National Measurement Laboratory consists of four divisions with a total permanent staff of about one hundred which is augmented by approximately fifty guest scientists.

The Center for Chemical Physics (CCP), (1) develops and maintains the scientific competences and experimental facilities necessary to provide the nation with measurement methodologies and measurement services in the areas of thermochemistry, chemical kinetics, surface science and molecular spectroscopy; (2) measures, compiles, critically evaluates, and disseminates reference data to the industrial, government, and academic communities nationally and internationally; (3) develops theoretical methods and concepts, predictive equations and models; (4) develops standards and techniques of measurement; (5) provides federal, state and local governments, industry and the academic community with essential standards and certified standard reference materials needed to maintain the integrity of the measurement system; (6) provides consultative services and participates in collaboration efforts with other NBS Centers and the outside community.

The summary of activities is organized by division: Surface Science, Chemical Kinetics, Chemical Thermodynamics and Molecular Spectroscopy. The report of each division is divided into: (1) an introductory discussion of the objectives and programs of the division; (2) a review of all projects which includes accomplishments and future plans; (3) lists of outputs and actions which indicate in a quantitative way the activity and accomplishments of the division.

A detailed table of contents has been provided. It will permit the reader to find those activities of greatest interest. More information about particular work may be desired. To obtain this, the reader should address the individual scientists or their division, c/o Center for Chemical Physics, Chemistry Building, B-162, National Bureau of Standards, Gaithersburg, MD 20899. Telephone extensions are listed in the table at the end of the report (301-921-EXT).

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SURFACE SCIENCE DIVISION

C. J. Powell, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

1. INTRODUCTION

A. Background

Over the last ten years, there has been a dramatic growth of surface science and its applications. At the national and local meetings of many professional societies, there are typically multiple sessions of papers concerned with the physical and chemical properties of surfaces. Similarly, many current professional journals and books are devoted in whole or in part to similar reports of recent advances in this field. These advances result from investigations of basic properties (such as composition, atomic structure, electronic structure) of surfaces and the dependence of many complex surface processes (such as molecular sticking, dissociation, diffusion, reaction, and desorption) on the basic properties and other variables relevant to catalysis, corrosion, thin-film systems, microelectronics, computer elements, and communications applications. Investigations of this type range from fundamental studies, at an atomic and molecular level, on clean single-crystal surfaces to similar studies on appropriately modified surfaces or structures and lead not only to the development of surface science but also to new materials, devices, and processes. Similar investigations, principally measurements of surface composition and of other needed properties, are frequently made of a large variety of materials (e.g., metals, polymers, semiconductors, oxides, glasses, etc.) after fabrication and at various time during their service life for quality control, process optimization, and failure analysis. The growth of surface science and its multidisciplinary impact on many important technologies have been documented in a recent article by H. D. Hagstrum [Frontiers in Science and Technology, W. H. Freeman and Co., New York (1983), pp. 113-134].

A large number of techniques are utilized for surface characterization. A choice of one or more techniques is made typically on the basis of the property to be measured, the specimen material, and the specific needs (e.g., spatial resolution, chemical information, sensitivity, degree of difficulty, and cost). The most common type of surface measurement is the determination of surface composition. Most surface analyses now are qualitative but there is a growing demand for quantitative analyses with improved accuracy. At the present time, there are very few standard procedures and limited reference data and reference materials. A variety of techniques is employed for the determination of surface atomic

structures, surface electronic structure, and for investigations of surface processes such as reactions, diffusion, segregation, etc. Theories of the measurement process need to be developed for the newer techniques. For all techniques, there is a need for relevant procedures, tests to establish measurement reliability, and applicable reference data. In most cases, the measurement science needs to be developed since knowledge of the key concepts and parameters is often extremely limited.

The techniques utilized in surface science have generally been applied to characterize surfaces in an ultrahigh vacuum environment. The solution of many scientific and technical problems often requires removal of liquid- or gas-phase material prior to surface examination and/or the removal of solid-phase material to expose a region of interest. While this approach has often been successful, artifacts of many different types can arise during the removal of one or more phases. There is therefore a growing need for improved measurement methods that can be used for the in situ characterization of solid-solid, solid-liquid and solid-gas interfaces with the sensitivity, elemental specificity, and spatial resolution comparable to those attained with the current surface-characterization methods.

B. Goal, Objectives and Division Program

The goal of the Surface Science Division is to improve the quality of existing surface-characterization measurements and to extend the present capability. Specific objectives of the Division are:

- (1) Perform experimental and theoretical research in surface science to provide a scientific base for surface-measurement methodology;
- (2) Develop measurement methods and provide properties data for the physical and chemical characterization of surfaces and surface processes to meet identified needs of industry, government, and other groups;
- (3) Develop standard procedures, calibration data, and reference materials in cooperation with national and international standards organizations; and
- (4) Develop expertise in selected new areas of science in order that NBS can provide measurement services where needs are anticipated in the near future.

Objectives (1) through (3) are met organizationally through an NBS task titled "Development of Measurement Methods for Surface Properties" (Task 15502). The Division's program for this task is divided into two principal activities, a Surface Standards Program and a Surface Measurements Program. Work performed during the year in these two areas is reported in Sections 2 and 3, respectively. This work is supported by

NBS resources (including some funds transferred through the Office of Standard Reference Data) and by contracts with two Federal agencies (Department of Energy and Office of Naval Research).

Objective (4) is met through the Surface Competence Program (Task 26117). This task was established in October, 1984 and represents a new focus by the Division in two areas, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". A separate report on these activities is given in Section 4.

C. Technical Output and Professional Interactions

Sections 5 and 6 of this report contain listings of the publications and talks, respectively, for the past year by Surface Science Division staff and for projects supported by the Division.

Many members of the Division staff hold leadership positions in professional societies and groups, as listed in Section 8. These interactions not only reflect the professional esteem in which these staff members are held but provide useful mechanisms for both disseminating the results of NBS work and for learning of significant measurement problems being faced by those using surface-characterization equipment.

Interest in surface science and surface characterization at NBS continues to grow. The Division has had an active Seminar program, as indicated in Section 7, and these seminars have been attended by other NBS staff. The Division staff also participates in an informal weekly lunch meeting, attended by scientists from a number of NBS organizational units, at which developments in surface science are discussed. Members of the Division staff are frequently consulted on a wide range of NBS problems.

Much of the Division's work is carried out in collaboration with other scientists within NBS, within the U.S.A., and internationally. The nature of these collaborations is shown in Section 9. These collaborations are considered important because they enable a relatively small Division staff to work synergistically with other experts, they enable us to have access to unique facilities or expertise, and they enable our expertise to be extended to a larger range of important scientific and technical problems.

The Division has been fortunate in having thirteen visiting scientists work at NBS for varying periods during the past year, as indicated in Section 10. These scientists enrich our staff and our projects. A further enrichment of our programs comes from Postdoctoral Research Associates who hold 1- to 2-year appointments; four Postdoctoral Research Associates worked in the Division during FY 1985.

2. SURFACE STANDARDS PROGRAM

G. P. Chambers, W. F. Egelhoff, Jr., N. E. Erickson
J. Fine, Y. Hashiguchi, R. D. Kelley, C. J. Powell

The term "surface standards" is intended to cover a broad range of activities that are directed to improving the quality of surface-characterization measurements through: (1) development of needed reference data and standard reference materials; (2) leadership in standards-committee activities, the development of standard practices, and other actions to improve the accuracy and reliability of surface-analysis measurements; and (3) publication of review articles and books that enable scientists to make surface-characterization measurements of the needed quality.

A. Reference Data

We describe here results of projects in which needed reference data are being generated. Section 2.C includes recent review articles by Division staff that summarize and evaluate data required in a number of surface spectroscopies.

1. Sputtering Yield Data Compilation (J. Fine and G. P. Chambers)

Sputtering techniques for depth-profile analysis are presently being used in conjunction with a number of surface analytical methods to analyze compositional changes of materials at surfaces and at interfaces. Many of these techniques have now progressed to the point of being able to provide quantitative sputter-depth-profile information yet the necessary sputtering yield data is not readily available in easy-to-use, evaluated form.

We are preparing a compilation of evaluated sputtering-yield data for those parameters that will have specific use in surface analysis and depth profiling. This work is supported by the NBS Office of Standard Reference Data. Our compilation will be in tabular form for those ion species (Ne, Ar, Kr, Xe, O₂, N₂, Cs) and energies (0.5 to 20 keV) and angles of incidence used in surface characterization. The compilation will contain sputtering yields for elemental targets only.

The HP-1000 Data System in the Center for Chemical Physics is being used for the data compilation. Dr. D. Neumann and members of his group have provided guidance as well as technical assistance with the software development.

Two interactive data-base management programs were developed this past year to handle the specific needs of the data compilation. The structure developed allows easy data entry into one of these data bases;

information can then be transferred to the second data base for rapid access and searching. Additional software has been written to sort and tabulate the searched data in a format suitable for publication.

Sputtering yield papers are being compiled; data has been abstracted and entered into the data-base system. Initial tests indicate that the system is operating properly. Work also is progressing on our on-line abstract searching capability so that we can collect and enter additional references and data directly from the computer search into our data base.

In the coming year we intend to complete the data searching and data entry, to evaluate the data set, and to compile sputtering-yield data of interest to the surface-analysis and sputter-depth-profiling community on elemental targets.

2. Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer (N. E. Erickson, C. J. Powell)

Knowledge of the specimen area being analyzed is important in surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), particularly when inhomogeneous specimens are being examined and experimental conditions are being varied. We have characterized the imaging properties of a commercial double-pass cylindrical-mirror analyzer (CMA) used for AES and XPS with extensions of a method developed elsewhere. These extensions have yielded more quantitative analyzer characterization than was possible previously. This work was motivated also by the need to evaluate the analyzer imaging properties on the binding-energy measurements described in Section 2.A.5 below.

The electron beam from the coaxial electron gun of the CMA was rastered across a test surface and the intensity of elastically scattered electrons detected by the analyzer was stored in a computer as a function of beam position on the specimen and other experimental parameters. The intensity data could be later plotted to give "three-dimensional" images that showed clearly the imaging properties of the CMA. Elastic-peak images have been obtained for a typical specimen orientation (in our case at an angle of 60° to the CMA axis) and for typical measurement conditions (electron energies of 100, 500, and 1000 eV; analyzer pass energies of 25, 50, and 100 eV; selection of small or large apertures intended for AES or XPS measurements, respectively; and for selected analysis energies ranging between 1.5 eV above the incident energy and up to 5 eV below the incident energy). We have investigated how the images were modified as the specimen was translated along the CMA axis about its optimum position. Finally, we have obtained absorbed-current images to ensure that the test specimen was sufficiently smooth to prevent significant artifacts occurring in the elastic-peak images.

Figure 1 shows examples of elastic-peak images recorded with the specimen at its optimum position and with use of the AES aperture. Figure 1(a) shows images at a fixed pass energy of 50 eV and for incident energies of 100, 500, and 1000 eV; Figure 1(b) shows images for an incident energy of 500 eV and pass energies of 25, 50, and 100 eV. It is clear that the specimen area contributing to the detected signal is changing as these operating parameters are varied.

Comparisons have been made of observed image widths for particular operating conditions with those expected from a simple analysis. Semi-quantitative agreement has been obtained although there are differences in trends (as a function of electron energy or analyzer pass energy) that can be associated with non-uniformities of grids on the inner-cylinder apertures, with lack of sphericity of the retarding grids, and with simplifications of the analysis. Asymmetries in the measured images, for example at high retardation ratios or when the specimen is moved from its optimum position, are due to specific imperfections in our instrument.

Substantial changes are seen in the elastic-peak image shapes as the specimen is translated along the analyzer axis to simulate accidental misalignments. Similar changes are obtained in the image shapes as an offset voltage is applied to the electron gun so that the analyzer detects electrons on the high-energy side of the elastic peak or electrons that have been inelastically scattered in the specimen. The latter changes can be qualitatively interpreted in terms of the known coupling between detected signal and source position, angle of emission, and electron energy. These results indicate that sharp peaks in an energy distribution come from a smaller specimen area than for broad peaks or for inelastically scattered electrons.

We have also measured changes in the position of the elastic peak as the incident beam is deflected to representative points on the specimen in the field of view of the analyzer. Changes of up to ± 0.15 eV in peak position were found and these were not symmetrical about the vertical as would be expected for an ideal instrument.

It is planned to draft a Recommended Practice for Characterization of the Imaging Properties of Electron Energy Analyzers for ASTM Committee E-42 on Surface Analysis based on the above methods.

3. Energy Dependence of Electron Attention Lengths (C. J. Powell)

The attenuation length (AL) of low-energy electrons in solids is an important parameter in surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). The AL determines the surface sensitivity of AES and XPS (and other electron-spectroscopic techniques of surface characterization) and is required for quantitative surface analysis by AES and XPS. Accurate AL

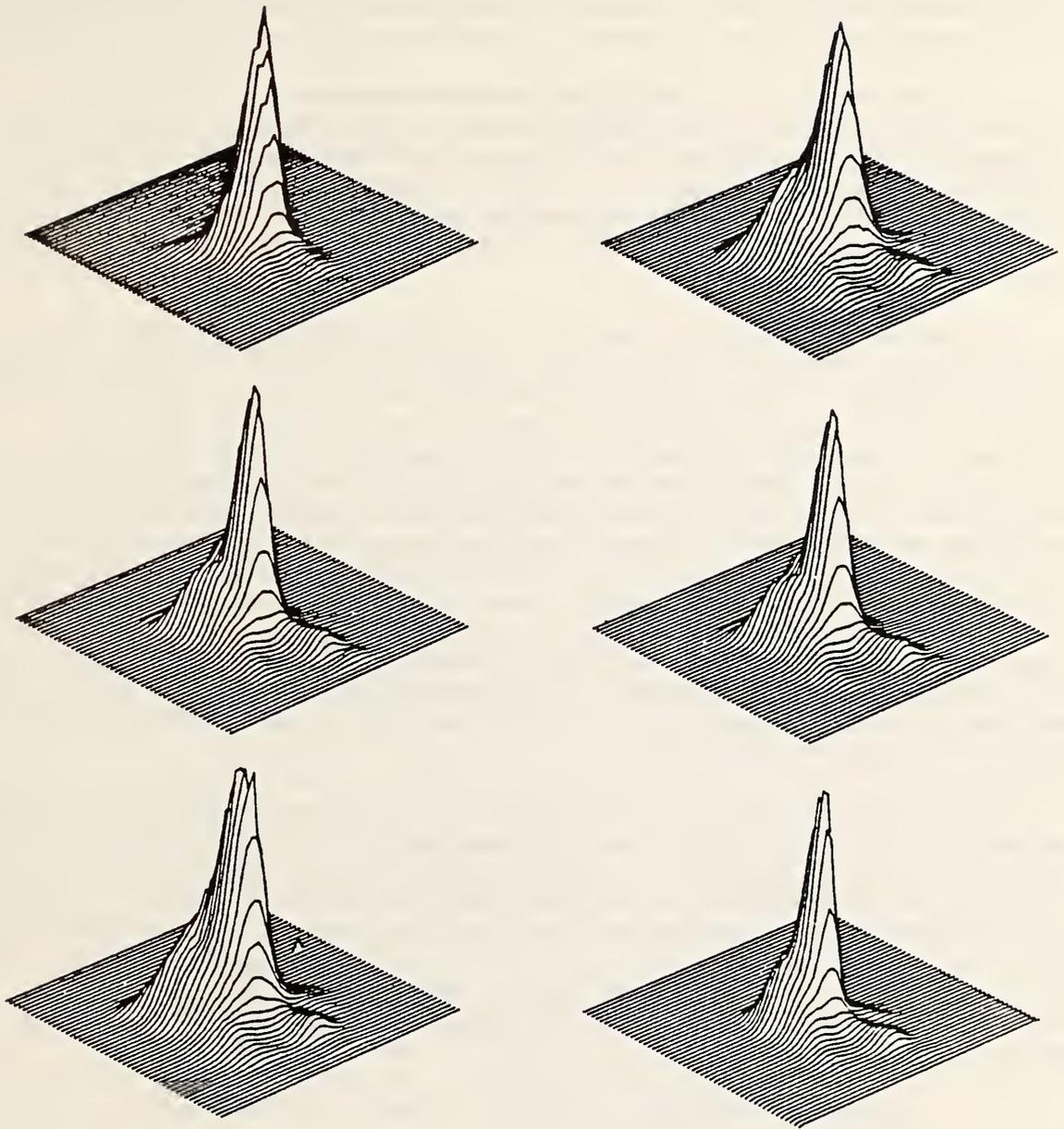


Fig. 1 Elastic-peak images recorded with a double-pass cylindrical-mirror analyzer, the AES aperture, and a test specimen at its optimum position. Left: Images recorded with an analyzer pass energy of 50 eV and incident energies of 100 eV (top), 500 eV (center), and 1000 eV (bottom). Right: Images recorded with an incident energy of 500 eV and analyzer pass energies of 25 eV (top), 50 eV (center, and 100 eV (bottom). The horizontal (bottom left to right) distance scanned by the electron beam on the specimen is 13 mm and the vertical distance is 15 mm.

measurements are difficult in the electron energy range of practical interest but relative AL measurements are useful since they give the AL energy-dependence which is needed in one method of quantitative analysis.

The Bethe theory of inelastic electron scattering in matter has been very successful and it was thought useful to test whether it was valid also for AL data in solids. According to the Bethe theory, AL values λ would be given by the formula, $\lambda = AE/b \ln(cE/\Delta E)$, where E is the electron energy, ΔE the most probable excitation energy for the material, A a term containing material and other constants, and b and c parameters of order unity.

AL measurements for Al, Au, Si, Ge, Al_2O_3 , SiO_2 , NaF, NaCl, and KI have been successfully fitted to the Bethe formula for E typically between 100 and 1500 eV. The quality of these fits was generally superior and the electron energy range greater than for earlier fits to an empirical formula. It was found, however, that the parameter b was higher and the parameter c much lower than the values expected from theory. These deviations are similar to those found in other tests of the Bethe theory where the electron energies were not high enough for the parameter values to reach their asymptotic values. Nevertheless, it is useful empirically that the Bethe equation adequately describe those AL data which exist for a representative group of materials over a substantial energy range. Although the derived values of the parameters are material-dependent, good estimates of the ratios of ALs at different electron energies can be obtained from the Bethe equation using the average value of $c = 0.4$ and the average value of $\Delta E = 20$ eV.

A separate investigation has shown that electron inelastic mean free paths (IMFPs) can be calculated from experimental dielectric data. IMFPs calculated for eight materials agreed reasonably (within 50%) with available AL measurements (which had been obtained with a model in which elastic electron scattering was assumed to be insignificant). Since it is difficult to measure ALs with accuracies much better than about 50%, it is useful to obtain IMFP data from another base of experimental data. It is planned to extend these calculations using optical data for additional materials.

4. Atomic Layer-by-Layer Analysis of the Source of Angular Anisotropies in XPS and AES (W. F. Egelhoff, Jr.)

Attenuation lengths of low-energy electrons in solids, important for quantitative surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), have been frequently measured from the characteristic decay or growth of an AES and XPS signal as a film of increasing thickness is deposited on a substrate. A fundamental complication for such measurements is the enhancement of an AES or XPS peak intensity along crystal axes in single-crystal samples. These enhancements along nearest-neighbor directions are due to forward

scattering of the emitted electrons by lattice atoms. An example of the angular anisotropy is shown in Figure 2(a) for epitaxial Cu layers on Ni(100).

In order to deepen the understanding of the depth dependence of this forward-scattering phenomenon, single-scattering electron-diffraction calculations have been performed in collaboration with Dr. R. A. Armstrong of the National Research Council, Ottawa. Figure 2(b) shows an example of these calculations for conditions appropriate to the data in Figure 2(a). The comparison between the calculations and the data reveal several important points.

(1) Since all observed peaks are accounted for in the calculations, single-scattering events must be the dominant mechanism for the observed peaks.

(2) The observed thickness at which each of the four peaks first appears is in accordance with predictions of the calculations. This result confirms the original interpretation, namely that the intensity of the peaks is due mainly to constructive interference in the forward scattering direction by nearest-neighbor and next-nearest-neighbor atoms in the lattice.

(3) The calculated enhancement in the peak intensities continues to grow for Cu thicknesses greater than 3 ML whereas in the data there is very little increase beyond a thickness of 3.3 ML. (Compare, for example, the peak at 45° in Figures. 2(a) and (b).) This comparison reveals an important result. The first (single) scattering event enhances the intensity along a nearest-neighbor direction (e.g. at 45° in Figure 2(c)) but subsequent (multiple) scattering events wash out this enhancement. The single-scattering calculations thus predict a continued growth in the peaks which is not observed experimentally. As a consequence, the measured peaks are due more to short-range order, or nearest-neighbor axes, than originally thought.

This combined theoretical and experimental analysis has deepened the understanding of the phenomena involved in electron attenuation-length measurements with single-crystal materials. Such measurements will have to be made in the future for specific angles of electron emission.

5. Measurement of Core-Level Binding Energies (N. E. Erickson and C. J. Powell)

Accurate reference values of the binding energies of core-level electrons are needed for the commonly used technique of x-ray photoelectron spectroscopy (XPS) and for other surface-characterization methods. These values are needed for the calibration of instrumental energy scales. For this application, data are required for a limited number of pure materials that adequately cover the range of common measurements.

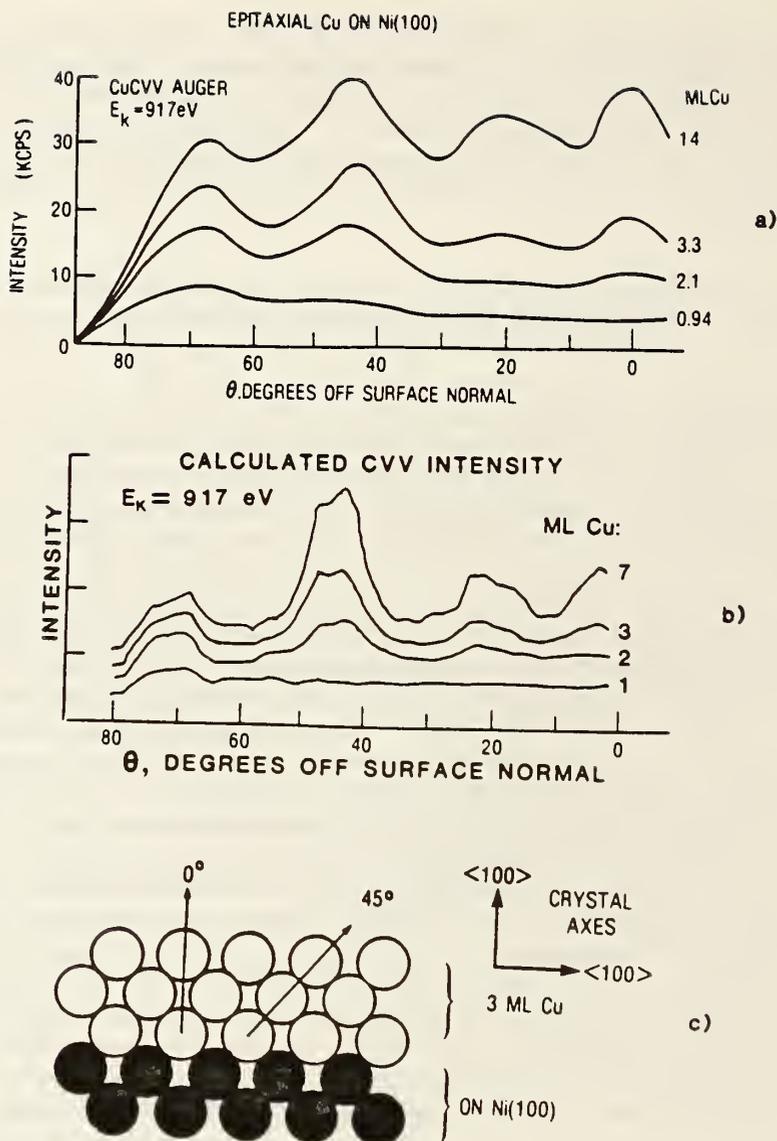


Fig. 2. (a) Measured intensities of the x-ray-induced Cu L_3VV Auger intensity as a function of polar angle of emission for various thicknesses (in monolayers) of Cu on Ni(100). (b) Corresponding calculated intensities. (c) Schematic illustration of the surface profile.

We have made measurements earlier of the core-level binding energies by XPS for the principal peaks of Ni, Cu, Ag, and Au. The accuracy of these measurement, however, was limited severely by voltage drifts in our XPS system. To improve the accuracy and precision of the measurements, we have installed programmable power supplies and digital multimeters for the control and measurement of the voltages applied to the cylindrical-mirror analyzer. The experimental measurements are under computer control. Programs have been written to set and step the analyzer voltage suppliers and to read the multimeters. Least-squares peak-fitting routines have been evaluated for determining peak positions. These tests have shown that fits using a quadratic or a quartic to the top 20-50% of a peak are about equally satisfactory.

Stability checks have been made to assess the short-term (several hours) and long-term (ca. 1 month) stability of the upgraded system. The short-term reproducibility in the location of peaks is now about 4 meV and is limited by the counting statistics of typical scans. The long-term stability is approximately 10 meV and is within the instrumental specifications for electronic drift.

A certified calibration of the voltage-measuring instruments is scheduled to be made shortly. We will then make new high-accuracy measurements of the Ni, Cu, Ag, and Au XPS peaks and compare these with recent independent measurements at the U.K. National Physical Laboratory (NPL). We will initially use a beam of elastically scattered electrons from a gun with a thermionic cathode as an energy reference, as we have in our preliminary measurements. We will then use a gun with a field-emission cathode to compare results from the two types of electron sources and to resolve an apparent discrepancy in a recent measurement of the Au $4f_{7/2}$ binding energy made using a field-emission reference source. After completion of these XPS binding-energy measurements, we will make similar measurements of the kinetic energies of Auger electrons from Cu, Ag, and Au and compare these results with similar measurements now in progress at NPL.

6. Reference Data for X-ray Photoelectron Spectroscopy and Auger-Electron Spectroscopy
(C. J. Powell and N. E. Erickson)

A project was initiated in FY 82 with funding by the NBS Office of Standard Reference Data to prepare compilations and evaluations of core-electron binding energies and of the kinetic energies of selected Auger electrons for a wide range of elements and compounds. In particular, data are being compiled of the "chemical shifts" that can give useful information on the chemical state of a particular element. Data of this type are now scattered throughout the scientific literature but there is a need both for a convenient single source and for evaluation of the sometimes conflicting data. The reference data are being compiled by Dr. C. D. Wagner, a contractor to NBS, and the Surface Science Division is providing technical review. Dr. Wagner has currently generated over 10500 data entries in his files from 600 papers and the compilation is

approximately half-completed. During the past year, progress has been significantly delayed by illness but it is expected that the project should be completed next year. The reference data will be included in a report for the Journal of Physical and Chemical Reference Data.

7. Algorithm for Fitting Sputter-Depth-Profiles at Interfaces (J. Fine, G. P. Chambers, and Y. Hashiguchi)

The determination of interface widths from sputter-depth-profiles is presently accomplished by means of graphical methods. Since the shapes of such interface profiles are generally not symmetric and since there is no accepted method of measuring interface widths, accurate width determination as well as intercomparison of results is often difficult to accomplish. One solution to this problem is to fit numerically the interface profile shape to an appropriate analytical expression from which one can obtain a factor proportional to different definitions of the interface width.

In collaboration with Dr. W. H. Kirchhoff of the NBS Chemical Thermodynamics Division, a fitting analysis for Auger-electron sputter-depth profiles has been developed using a logistic function of the form:

$$I = [A + a(T-T_0)]/(1 + e^{-t}) + [B + b(T-T_0)]/(1 + e^t)$$

where I is the peak intensity of the Auger spectrum of the sputtered atom as a function of time T . A is the intensity from a totally covered surface, B is the background intensity from a completely uncovered surface, and a and b empirical parameters which can account for additional time dependence of instrumental effects. T_0 is the apparent midpoint of the transition region and t is a dimensionless, reduced time defined as $(T-T_0)/D$. The scaling factor, D , is the characteristic time for sputtering through the interface region. Asymmetry in the depth profile can be accommodated by allowing D to vary with time.

A least-squares fitting program has been written which fits the measured Auger spectral intensities to the above equation within measurement error. All currently used measures of the interface width are proportional to D . The statistics associated with the least squares fit allow confidence limits to be placed on the measured widths of interface regions and on the widths of surface layers of dissimilar materials.

8. Needs for Reference Data

The growth of surface science and its applications has led to needs for expanded reference data. These needs can be summarized in the following three categories.

(a) Surface Analysis

Four techniques are now in common use for surface analysis: Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and ion-scattering spectroscopy (ISS). With each technique, there is need for the following reference data:

- evaluation of spectra from pure elements for common conditions of measurement
- evaluation of chemical or matrix effects on spectra
- benchmark data for the calibration of the energy and intensity scales of instruments
- reference data on line positions in compounds
- reference data for key parameters in quantitative analysis (e.g., ionization cross sections (AES, XPS), ion scattering cross sections (ISS), electron inelastic mean free paths and attenuation lengths (AES, XPS), electron backscattering (AES), ion neutralization cross sections (SIMS, ISS), and multiple ionization (SIMS))
- algorithms for data analysis (e.g., determination of background due to multiple scattering (AES, XPS, ISS) and fragments (SIMS, ISS), deconvolution to obtain source lineshape (AES, XPS, ISS), inelastic scattering (AES, XPS), and double scattering (ISS))
- data for ion sputtering yields in elements, alloys, and compounds as a function of ion type, ion energy, and bombardment geometry
- data for radiation damage rates during analysis, including cross sections for desorption from surfaces and decomposition of surface layers.

(b) Surface Science

Many techniques are in common use for the determination of surface properties and processes. Data are needed in the following areas:

- reference data on vibrational energies and intensities for molecular species on surfaces (as measured by electron energy-loss spectroscopy, infrared spectroscopy, Raman scattering, neutron inelastic scattering)

- reference data for determination of surface structures by low-energy electron diffraction and other techniques (e.g., library of basic data, algorithms to compute surface structure)
- reference data for absolute determination of surface coverages (atoms/cm²) on surfaces of different structure and atomic composition
- reference data for surface processes (kinetic data for catalytic and surface reactions, desorption, diffusion, segregation)
- Ion-surface interactions are of importance in sputtering and ion scattering spectroscopy. Reference data are needed to characterize the electron and photon spectroscopy of scattered and sputtered ions, as well as of excited neutral species leaving the surface.

(c) Interface Science

There is rapid development now of techniques that can be used for the in situ characterization of solid-solid, solid-gas, and solid-liquid interfaces. A variety of techniques (e.g., Rutherford backscattering spectroscopy, infrared spectroscopy, Raman spectroscopy, extended x-ray absorption fine structure, neutron inelastic scattering, particle-induced x-ray emission) are being utilized and reference data and algorithms will be required for their effective application.

The Division is providing reference data to meet some of the above-mentioned needs through the projects described in this Section and through the publication of the review articles listed in Section 2.C. Other current Division projects, not described in detail in this report, are:

- comparison of core-level excitation energies by different spectroscopic techniques
- calculation of electron inelastic mean free paths from experimental optical data
- measurement of electron attenuation lengths in condensed molecular films

The Division will coordinate its efforts with the data activities that have been initiated recently through the Surface Chemical Analysis activity of the Versailles Project on Advanced Materials and Standards (VAMAS), as described in Section 2.D.2. There will also be coordination with the NBS Office of Standard Reference Data and the Standard Reference Data Subcommittee of ASTM Committee E-42 on Surface Analysis.

B. Reference Materials

1. Development and Production of Standard Reference Materials for Sputter-Depth Profiling (J. Fine)

The objective of this project is to develop standard reference materials (SRM's) that will allow convenient determinations of ion-beam sputter-removal rates in commonly used surface-analysis instrumentation. Thin-film reference materials of known thickness will be used to calibrate ion-gun current densities for particular operating conditions. This information together with sputtering-yield data for a range of materials will establish depth scales in the measurement of depth profiles.

Prototype thin-film structures were initially fabricated in order to evaluate their usefulness as depth profiling SRM's and to develop appropriate characterization techniques. These structures were made by sputter deposition as part of a joint US/Yugoslavia program between NBS and Dr. B. Navinsek at the J. Stefan Institute in Ljubljana. Analyses of these prototype materials at NBS and by members of ASTM Committee E-42 on Surface Analysis were done using Auger-electron spectroscopy, x-ray fluorescence, secondary-ion mass spectroscopy, Rutherford backscattering spectroscopy, and proton-induced x-ray emission. The results were satisfactory and a stock of similar thin-film SRM's were fabricated in 1982 using the sputter deposition facility at the J. Stefan Institute in Ljubljana. Production and characterization of the Ni-Cr thin-film SRM was supported by the NBS Office of Standard Reference Materials.

The preliminary analyses obtained on the nickel-chromium multilayered thin-film structures indicate that this material should be of considerable benefit as a depth-profiling SRM. Work on its characterization and calibration has now been completed. We have determined the uniformity and periodicity of the thin-film layers, absolute film thicknesses, sputtered interface depth resolution, and structural stability. Measurement methods used to characterize this Ni-Cr SRM include N(E) Auger sputter profiling, Rutherford backscattering spectroscopy (RBS), and neutron activation analysis (NAA). These measurements have resulted in the following certified values for this Ni/Cr structure that has recently been issued as NBS Standard Reference Material 2135.

(a) Total Cr and total Ni thicknesses

The total thickness of the five Cr layers and the total thickness of the four Ni layers were determined by NAA using a gravimetrically calibrated reference and are given below.

<u>Element</u>	<u>Total Thickness</u>		<u>Uncertainty</u>
Cr	191	$\mu\text{g}/\text{cm}^2$	$\pm 8 \mu\text{g}/\text{cm}^2$
Ni	235	$\mu\text{g}/\text{cm}^2$	$\pm 9 \mu\text{g}/\text{cm}^2$

The uncertainty stated is based on our best judgement of all factors involved and corresponds to about two standard deviations of the average.

- (b) Individual layer uniformity and Ni+Cr bilayer uniformity (periodicity).

Layer thickness uniformity was determined by measuring the ion bombardment time required to sputter-remove a single layer. This time was obtained by monitoring the surface composition by Auger spectroscopy during sputter erosion. The uniformity of Ni+Cr bilayer removal also was determined in a similar way.

<u>Type of Layer</u>	<u>Relative Layer thickness uncertainty*</u>	<u>Number of profile measurements (9 layers each)</u>
Single Cr layer	± 4.8%	6
Single Ni layer	± 4.6%	6
Bilayer of Ni and Cr	± 3.0%	6

*This uncertainty is two relative standard deviations.

- (c) Individual layer thicknesses

The average thickness for a single layer of a given element was obtained from the total layer thickness for that element and the number of layers present. The relative uncertainty of this average layer thickness was determined by combining the uncertainties in the total thickness and in the single layer uniformity for that element.

<u>Element</u>	<u>Single layer thickness</u>	<u>Relative layer thickness uncertainty*</u>
Cr	38.2 $\mu\text{g}/\text{cm}^2$	± 2.3 mg/cm^2
Ni	58.8 $\mu\text{g}/\text{cm}^2$	± 3.5 $\mu\text{g}/\text{cm}^2$

*This uncertainty is two standard deviations

The following additional information has been provided about SRM 2135; this information is uncertified.

- (a) Layer thicknesses in units of length

The certified layer thicknesses could be converted into units of length (nm) if the densities of the layers were known. As these densities are not known, an approximate thickness in nm can be derived by using the known bulk densities for Cr (7.19 g cm^{-3}) and Ni (8.9 g cm^{-3}); the values so obtained are 53 nm for Cr and 66 nm for Ni.

(b) Layer thickness and uniformity

Measurements of SRM 2135 using RBS give information on the single-layer thickness and uniformity of each of the Cr and Ni layers. RBS measurements of the single-layer uniformity confirm the uncertainties obtained from the sputter removal times for single layers. Layer thickness measurements obtained by RBS depend on the value of the stopping power used to calculate thickness. A 5 to 10% uncertainty in thickness can result from the uncertainty in currently available stopping-power data and can limit the accuracy of this technique. Single-layer thickness determined by RBS confirm the values certified, providing that a 5 to 10% uncertainty is assumed in the RBS measurements. The RBS result obtained for the average thickness of a single Cr layer is 8.5% smaller than its certified value, while the RBS single Ni value is 5.4% smaller than that certified.

(c) Relative sputtering rates and yields of Ni and Cr using argon ion bombardment

Ion Energy (keV)	Ni/Cr Rate	Ni/Cr Yield
1.0	1.03	1.12
2.0	1.07	1.17
3.0	1.09	1.20
4.5	1.09	1.20

Rate is expressed in units of length/time.

Yield is given as number of atoms sputtered per incident ion.

Future work includes characterizing and certifying additional Ni/Cr structures similar to SRM 2135 as well as a "marker" layer-type sputter depth profile SRM which we have recently fabricated in production quantities. This material also was fabricated in Dr. Navinsek's laboratory and consists of eight Cr layers (~ 40 nm each) separated by about 2 monolayers of Cr_2O_3 .

2. Quantitative Sputter Depth Profiling of Interfaces
(J. Fine, Y. Hashiguchi)

Determination of composition-versus-depth at virgin solid/solid interfaces is at present difficult to achieve with sputter-depth-profiling techniques. This is due, to a large extent, to a lack of understanding of bombardment conditions (i.e., ion beam energy, species, angle of incidence, current density, and sputtered depth). A careful evaluation of such factors which affect interface resolution is not available for any given interface system. A consistent set of such measurements obtained for various ion beam parameters, all done on the same material, would significantly enhance our ability to assess the abruptness of interfaces before sputter-profile analysis took place and would be of value in determining optimum sputter-profile conditions.

Our development of the Ni-Cr thin-film depth-profile SRM 2135 with known layer thickness and periodicity (as described above) makes it both possible and practical to examine systematically the dependence of interface resolution on ion beam parameters. Use of the computer controlled, sequential-mode N(E) Auger data system which has been previously developed allows us to obtain reliable and accurate measurements of the interface depth resolution for the Ni-Cr material.

In collaboration with Dr. P. A. Lindfors of the Perkin Elmer Corporation, Physical Electronics Division and Dr. D. F. Mitchell of the National Research Council of Canada, Ottawa, we have examined the dependence of Ni-Cr interface broadening on ion beam energy, ion current density, and angle of incidence, all as a function of sputtered depth. Our results indicate that much narrower interfaces are observed when profiling with low-energy ions; for example, the interface widths with 1 keV argon ion bombardment at a particular ion-beam angle of incidence are about half those for 3 keV bombardment. We also find that narrower interfaces can be obtained by bombarding at more oblique (grazing) angles. Our narrowest interfaces (~ 5 nm) resulted when the ion beam was incident at 70° with respect to the surface normal.

Preliminary measurements of interface-width dependence on ion-beam current density indicate this parameter may affect interface resolution. We plan to explore this dependence by examining the relationship between ion current density and ion energy.

3. Needs for Reference Materials

The following needs for additional reference materials have been identified.

(a) Depth-Profiling SRM's

Surface analysis is frequently combined with ion sputtering to measure composition versus depth and to investigate solid-solid interfaces. It is believed that sputter-depth-profiling applications will continue to grow and, with the development of new techniques for deposition of materials (e.g., molecular-beam epitaxy), the development of better depth-profiling techniques, and demands for better accuracy, use of new materials, and desire for sharper interfaces, there will be an increased demand for suitable SRM's to ensure the reliability of the relevant measurement system.

NBS has recently developed a multi-layer periodically-modulated SRM consisting of alternate layers of Ni and Cr (Section 2.B.1). Similar structures consisting of Ni/Ag and Cr/Cr₂O₃ have been fabricated but remain to be characterized. We have also fabricated films of Ta₂O₅ on Ta and these also have to be characterized.

There are needs for similar SRM's involving other types of materials in high-technology industries, for example, SiO₂ on Si, epitaxial modulated-thickness films of GaAs/GaAlAs, thin layers of metals on semiconductors (Schottky barriers), and polymer films on metal substrates.

(b) Calibration of Surface Analysis Instruments

There is a growing need for the characterization and calibration of surface-analysis instrumentation, particularly since the newer computer-controlled instruments require greater system stability and reproducibility than before. Until recently, most surface analyses have been qualitative but there is increasing demand for quantitative analyses of defined accuracy. These developments require SRM's for instrument calibration (e.g., of the instrument transmission functions for Auger-electron spectrometers (AES) and x-ray photoelectron spectrometers (XPS) and for the determination of instrument performance (e.g., the detection of trace constituents).

Pure elemental and multicomponent materials can be utilized for calibration of the energy and intensity scales (and instrument transmission functions) of AES and XPS instruments. A suite of pure elements (e.g., Cu, Ag, and Au) could be used for both purposes. Liquid alloys (e.g., Ga-Sn or Ga-In) can be cleaned readily to generate two-component surfaces of known composition for checks of instruments and algorithms for analyses. Multicomponent materials with known quantities of trace elements are needed for determining the ability of an instrument to detect trace species. Suitable materials could include ion-implanted impurities in silicon (with a specified depth distribution and maximum concentration) and multi-component liquid alloys (with homogeneous compositions or with segregation of trace species at the surface).

(c) Surface Science

There is a need for SRM's that would lead, with the user following a prescription, to surfaces of known composition (e.g., to known coverage of a chemisorbed layer of molecules on a metal substrate or to a monatomic layer of a metal on a substrate). A single-crystal SRM (e.g., Ni) could be cleaned and exposed to different gases (e.g., O₂, N₂, H₂, CO, H₂S) to establish known surface coverages of such gases. Such an SRM would enable calibration of AES and XPS equipment now used for measurements of surface coverages. Another use of the SRM could be through the deposition of several monolayers of a metal (e.g., Ag), again after cleaning, with appropriate thermal treatment to remove all but a monolayer of the deposit. This process could also be used for the calibration of AES and XPS equipment used for investigations of novel properties of ultrathin metal films.

The Division will coordinate its activities to produce and characterize SRM's with related efforts that have been initiated in other countries through the Community Bureau of Reference of the Commission of the European Communities and, more recently, the Surface Chemical Analysis

activity of the Versailles Project on Advanced Materials and Standards (VAMAS), as described in Section 2.D.2. Plans for producing additional SRM's at NBS will also depend on sales of SRM 2135 (Section 2.B.1) and the results of a needs survey of the ASTM Committee E-42 on Surface Analysis.

C. Review Articles and Books

1. Review Articles

The Division staff authors many review articles and book chapters that provide information on measurement methods, relevant reference data, reference materials, theories of the measurement process for many surface spectroscopies, and surface standards.

Division staff members have authored 24 review articles recently. The titles and abstracts of review articles published since 1984 are listed below:

- (a) "Instrumentation for Photon Stimulated Desorption,"
R. Stockbauer, Nucl. Instr. Meth. 222, 284 (1984).

Photon stimulated desorption (PSD) refers to the ejection of ions, atoms or molecular fragments from a surface initiated by the absorption of single photons; to date, most studies have concentrated on detection of ions. The properties of PSD which make it attractive as a surface characterization tool are its extreme surface sensitivity, the ions being ejected only from the topmost layer and the rapidity with which the ions are ejected. Since the desorption is fast ($\sim 10^{-14}$ s), with respect to molecular vibrations ($\sim 10^{-12}$ s), the ion trajectory reflects the initial bonding geometry of the particle to the surface.

To study the ion desorption process, one would like to know the mass, kinetic energy distribution, angular distribution and the yield (desorption rate vs. photon energy) of the desorbing ions. Time-of-flight (TOF) analyzers are used where the time between the light pulses from the synchrotron light source is on the same order as the flight time of the ion from the surface to the detector. One can measure easily ion mass and yield but not kinetic energy or angular distributions with this class of analyzer. Electrostatic deflection analyzers are used to measure ion yields and kinetic energy distributions and, in some instruments, ion angular distributions. In general, they are useful where the time structure of the synchrotron light is too short to allow TOF analysis. Optical methods have recently been applied to the detection of excited states of neutral Li seen in PSD of LiF.

- (b) "Inelastic Scattering of Electrons in Solids," C. J. Powell, in Electron Beam Interactions with Solids for Microscopy, Microanalysis, and Microlithography, D. F. Kyser, H. Niedrig, D. E. Newbury and R. Shimizu, eds. (SEM Inc., Chicago), 19-31 (1984).

The principal mechanisms and available data for the inelastic scattering of electrons in solids are reviewed. The processes relevant for electron-probe microanalysis, electron energy-loss-spectroscopy, Auger-electron spectroscopy, and x-ray photoelectron spectroscopy are described and examples of relevant electron energy-loss data are shown. The discussion is based on the dielectric description of inelastic scattering and treats processes important in the excitation of both core electrons and valence electrons. Information is given on the cross sections for ionization of core levels, inelastic mean free paths of Auger electrons and photoelectrons in solids, and radiation damage.

- (c) "Non-adiabatic Effects in Elementary Surface Reactions: State-to-State Molecular Beam Experiments as a Probe," J. W. Gadzuk, in Many-Body Phenomena at Surfaces, D. Langreth and H. Suhl, eds. (Academic Press, N.Y.), 517 (1984).

A theory of elementary chemical reactions at solid surfaces is described in terms of surface-induced diabatic transitions between "reactant" and "product" potential curves. It is then shown how the internal vibrational state distribution of a diatomic molecule scattered from a surface could provide unique dynamical information required as input to the diabatic transition theory.

- (d) Early Applications of Vacuum, from Aristotle to Langmuir," T. E. Madey, J. Vac. Sci. Tech. A, 110 (1984).

Highlights of the development of vacuum science and technology from ancient times to the early twentieth century are reviewed. The view of the Greek philosophers that vacuum was an impossibility hampered understanding of the basic principles of vacuum until the mid 17th century. Verifiable vacua were first produced in Italy by Berti and Toricelli; von Guericke's dramatic experiments vividly demonstrated atmospheric pressure. Piston-like "air pumps" were widely used in England and the European continent through the 18th and early 19th centuries to produce and characterize the properties of vacuum (lack of sound transmission, inability to support life, gas discharges, etc.). The Industrial Revolution was made possible through the genius of Newcomen, who designed huge atmospheric engines (based on condensation of steam to form a vacuum beneath a piston, which was then driven by the pressure of the atmosphere). A system of "atmospheric railways" propelled by vacuum pistons was built in England in the mid 19th century. Serious scientific developments of the 19th century which necessitated vacuum included Crooke's and Faraday's gaseous discharge measurements, the first sputtering experiments by Grove, and isolation of the rare gases by

Ramsey, the standards work of Miller, the discovery of the electron by Thomson and of X-rays by Röntgen. The development of the incandescent light by Edison provided a background for the remarkable achievements of Langmuir in vacuum and surface science at the dawn of the 20th century. An appendix is included which lists museums containing vacuum-related exhibits.

- (e) "Laser Studies of Surface Chemical Reactions," R. R. Cavanagh and D. S. King, Chemistry and Physics of Solid Surfaces V, Springer-Verlag Series in Chemical Physics 35, 141 (1984).

A review of laser studies of surface chemical dynamics with emphasis on thermal desorption processes is presented. The correlation of gas-phase and liquid-molecular dynamics with analogous surface processes is demonstrated with primary emphasis on experimental techniques for monitoring relevant quantum state populations. Recent results for the desorption of NO from Ru(001) and NO from oxidized Ru crystals are compared in terms of rotational populations, and velocity and angular flux distributions.

- (f) "Characterization of Surfaces Using Electron and Photon Stimulated Desorption," T. E. Madey, D. E. Ramaker, and R. Stockbauer, Ann. Rev. Phys. Chem. 35, 215 (1984).

We review various mechanisms of electron- and photon-stimulated desorption of ions and neutrals from surfaces. Examples include desorption from ionic surfaces, from covalent adsorbates on metal surfaces, and from layers of physically adsorbed atoms. The use of the electron stimulated desorption ion angular distribution (ESDIAD) method for determining local structures of surface molecules is described.

- (g) "Inelastic Mean Free Paths and Attenuation Lengths of Low-Energy Electrons in Solids," C. J. Powell, Scanning Electron Microscopy/1984, IV, 1649 (1984).

A review is given of calculations of inelastic mean free paths and measurements of attenuation lengths of low-energy electrons in solids. The emphasis of the review is on the systematics of the dependence of these quantities on material and electron energy. Calculations of inelastic mean free paths from experimental dielectric data indicate that different dependences on electron energy occur in different materials and that deviations from simple theoretical or empirical expressions are to be expected.

- (h) "On Vibrational Lineshapes of Adsorbed Molecules", J. W. Gadzuk and A. C. Luntz, Surf. Science 144, 429 (1984).

The possible information content in lineshapes observed in vibrational spectroscopy of molecules adsorbed on surface is considered by drawing analogies with similar situations in other spectroscopic areas

where the systematics are more completely understood. When possible, simple physical models are introduced which illustrate the points to be stressed. Particular emphasis is placed on the relative roles of T_1 (dissipative decay) vs. T_2' (pure dephasing) processes in determining linewidths, on the roles of substrate electron-hole pairs, phonons, and photons in T_1 processes, and possible ways to establish which broadening mechanism is operative in a given situation. A particular kind of dephasing that is important for vibrational lineshapes in molecular crystals, so called exchange-coupling, is suggested as playing a significant role for molecular adsorbates as well. Some recent experimental studies are analyzed in the light of concepts introduced in this paper.

- (i) "The Thermal Desorption of Adsorbed Species," J. T. Yates, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 425 (1985).

The experimental and theoretical basis of thermal desorption spectroscopy as a tool for surface characterization is described. Methods of analysis of thermal desorption spectra to obtain kinetic information (desorption energies, desorption order, coverages of adsorbed species) are included, together with numerous examples of desorption of small molecules from single-crystal metal surfaces.

- (j) "Experimental Methods in Electron and Photon Stimulated Desorption," T. E. Madey and R. Stockbauer, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y. 1985), 465 (1985).

We review experimental techniques and applications of electron stimulated desorption (ESD) and photon stimulated desorption (PSD) of atomic, molecular, and ionic species from surfaces. The physical principles of these methods, as well as details of experimental measurements and data analysis are discussed. We close with a discussion of beam damage in surface analysis.

- (k) "Innershell Ionization Cross Sections," C. J. Powell in Electron Impact Ionization, T. D. Märk and G. H. Dunn, eds. (Springer-Verlag, N.Y.), 198 (1985).

A review is presented of cross sections for the ionization of inner-shell electrons by electron impact. Calculations, measurements, and empirical formulas are described and compared. Recommendations are given for the selection of cross-section data. Finally, applications of inner-shell ionization cross-section data to materials and surface analysis problems are described.

- (l) "The Coordinated Development of Standards for Surface Chemical Analysis", M. P. Seah and C. J. Powell, NBS Internal Report NBSIR 85-3120 (March, 1985).

This report is based on a proposal to the Steering Committee of the Versailles Project on Advanced Materials and Standards (VAMAS) for the coordinated development amongst the VAMAS member states of standards for surface chemical analysis. VAMAS was established following a meeting of the Heads of State or government at Versailles, France in 1982 that agreed on a number of projects relating to technology, growth, and employment. Specifically, VAMAS was organized to promote international coordination in the development of standards in a wide range of advanced material sectors. Surface chemical analysis was approved as a VAMAS Technical Working Area in June, 1984.

The report describes the growth and diversity of surface analysis in the development of advanced materials in modern technologies and the use of surface analysis for improved films and coatings. The principal techniques of surface analysis in common use are identified and the technical limitations to accurate surface analyses pointed out. Accurate surface analyses require: (i) knowledge of the principles of the measurement method, (ii) knowledge of the behavior of the measuring instrument, and (iii) correct interpretation and expression of the final measured result. Standards for the measurement of surface composition with known accuracy and for the reliable determination of chemical state require: (a) a base of principles, definitions of terms, and suitable equations, (b) reference procedures for the measurement of intensities and spectral features, (c) procedures and data for instrument calibrations, (d) reference data for material parameters such as elemental sensitivity factors, matrix terms, chemical state spectra, ion sputtering rates, etc; and (e) standard methods for specifying an analysis. Specific needs are identified for the common methods of surface analysis, Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and secondary-ion mass spectroscopy together with the needs for ion sputtering which is used to obtain composition versus depth information in films and coatings. Existing standards activities in the member countries of VAMAS are reviewed and suggestions are made for additional standards for surface chemical analysis.

- (m) "Surface Harpooning", J. W. Gadzuk, Comments on Atomic and Molecular Physics, 16, 219 (1985).

The principles involved in charge transfer/harpooning collisions between atoms or molecules and surfaces are presented in terms of concepts drawn from gas-phase atomic and molecular collision theory. As specific examples, the charge state of atoms and the vibrational excitation or dissociation of molecules which have experience harpooning while scattering from a surface are considered.

- (n) "The Uses and Limitations of ESDIAD for Determining the Structure of Surface Molecules", T. E. Madey, in The Structure of Surfaces, Springer Series in Surface Science 2, M. A. van Hove and S. Y. Tong, Eds. (Springer-Verlag, N.Y.), 264 (1985).

The principles and mechanisms of electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD), as well as the utility of the electron stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules, have been described in a recent book and several review articles. The present short paper is intended to provide a guide to the relevant literature, and to describe briefly some recent work relating to the uses and limitations of ESDIAD for determining the structure of surface molecules.

2. Review Articles in publication

We list below the titles and abstracts of review articles in the course of publication.

- (a) "The Chemisorption of Carbon Monoxide by the Transition Metals," J. T. Yates, Jr., T. E. Madey, and J. C. Campuzano, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, D. A. King and D. P. Woodruff, eds. (Elsevier).

A comprehensive review of the adsorption of carbon monoxide by transition and noble metals is presented. The systematics of CO adsorption and dissociation are discussed, along with detailed examinations of the surface structures, electronic and vibrational spectra, and kinetic behavior of adsorbed CO.

- (b) "Final-State Resolved Studies of Molecule-Surface Interactions," D. S. King and R. R. Cavanagh in New Laser and Optical Investigations of Chemistry and Structures at Interfaces, Verlag Chemie.

Quantum state-specific diagnostics as applied to surface dynamics are discussed. The NO molecule is used as an illustration of the experimental determination of gas-surface interactions. Topics reviewed included beam-surface scattering thermal desorption, vibrational accommodation, Doppler profiles, and Fourier-transform infrared emission spectroscopy.

- (c) "Core-Level Binding-Energy Shifts in Solids at Surfaces," W. F. Egelhoff, Jr., Surface Sci. Reports.

This review presents an overview of the theory and of various successful approaches to the interpretation of core-level binding-energy shifts observed in photoelectron spectroscopy. The

theoretical background is presented at a level readily accessible to the general reader. Particular attention is paid to relative merits of the two basically different conceptual frameworks for interpreting core-level binding-energy shifts, the initial-state--final-state approach and the equivalent-core-Born-Haber-cycle approach.

- (d) "Recent Advances Using ESDIAD: Applications to Surface Chemistry", T. E. Madey, C. Benndorf, N. D. Shinn, Z. Miskovic, and J. Vukanic, Proceedings of DIET-II Symposium (Desorption Induced by Electronic Transitions), in Springer Series in Chemical Physics.

Recent applications of ESDIAD (electron stimulated desorption ion angular distributions) to surface chemistry are described. Examples include the influence of catalytic promoters and poisons on surface structure and reactivity, the evidence for a new structural form for adsorbed H₂O (i.e., H₂O dimers on Ni(110)), and the characterization of a new bonding mode for CO on Cr(110). Calculations of the perturbing influence of image force and reneutralization effects in ESDIAD are described.

- (e) "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces", J. W. Gadzuk, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 4 of Methods of Surface Characterization (Plenum, NY).

An introduction to the theoretical basis of vibrational excitation mechanisms and processes relevant to vibrational spectroscopy of adsorbed molecules is presented.

- (f) "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces", R. R. Cavanagh, J. J. Rush, and R. D. Kelley, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr. and T. E. Madey, eds., Vol. 4 of Methods of Surface Characterization (Plenum, NY).

An introduction to neutron scattering as a probe of adsorbates at surfaces is presented. Emphasis is placed on experimental aspects of triple axis and time-of-flight techniques along with a single-phonon model for the spectral features. Wilson FG methods for constructing molecular force fields relevant to the molecular modes of the adsorbate are presented. The applicability of neutron scattering for exploring rotational diffusion and adsorbate torsions is also examined.

- (g) "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy", C. J. Powell, J. Vac. Sci. Tech.

An overview is given of recent developments in quantitative surface analysis by x-ray photoelectron spectroscopy and Auger-electron spectroscopy. The two major tasks of an analysis are the identification of the surface phases that are present and the determination of the concentrations of particular elements or compounds. Methods for accomplishing both tasks will be described together with the pitfalls and problems that remain. Particular attention is given to the following topics: identification of surface phases and reference data for the calibration of instrumental energy scales; reference data on inelastic mean free paths and attenuation lengths; effects of specimen crystallinity; intensity measurements; measurement of the imaging properties of electron energy analyzers; and the intensity-energy response functions of different instruments.

- (h) "Surface Chemical Analysis - Report on the VAMAS Project," C. J. Powell and M. P. Seah, Surf. Interface Anal.

The VAMAS project on surface chemical analysis is a multi-national cooperation for the provision of standards data and materials for surface chemical analysis measurement and for the provision of the basic understanding necessary for these activities. This project is one of a rapidly growing suite of projects initiated as a result of decisions following the 1982 Versailles Summit Meeting of the Heads of State or Government of Canada, France, Germany, Italy, Japan, UK, USA and the Representatives of the Commission of the European Community. During the past year national representatives to this VAMAS project have been appointed and national committees established. This article summarizes the philosophy, scope, and organization of the project and describes specific activities that have been initiated. Information is given on how individuals, both within and outside the group of member states, may participate.

- (i) "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra", J. W. Gadzuk, J. Electron Spectroscopy.

Extremely useful connections exist between the dynamics of adsorbed molecule vibrations, as revealed in spectroscopic lineshapes, and the dynamics of molecular processes at surfaces because in both cases, the constituent atoms of a molecule, solid, or combination of the two execute multi-dimensional motion over the same potential energy surfaces, undoubtedly sampling different regions of it.

In this paper, recent insights and advances in surface dynamics will be applied to the problem of vibrational lineshapes. Classical particle and semi-classical wavepacket dynamics will be used to address the issues of energy decay (T_1) vs. pure dephasing (T_2') overtones, and non-linear dynamics as they apply to lineshape analysis.

- (j) "Field Emission Microscopy - Trends and Perspectives," A. J. Melmed, Chemistry and Physics of Solid Surfaces VI, Springer-Verlag

The author's view of the role of surface microscopies, in particular the field emission microscopies, is given. Brief outlines of the historical development and nature of field-electron emission microscopy (FEEM) and field-ion microscopy (FIM) are given and selected examples are presented to illustrate the scope of research in FEEM and FIM. Research trends are described and some projections for the future are made.

3. Books

(C. J. Powell, T. E. Madey)

While there are many books and review articles on different aspects of surface science and its applications, there is a dearth of information on how to make reliable surface-characterization measurements. There is, in essence, a large information gap between review articles in which the latest scientific advances are discussed and manufacturers' handbooks in which the operation of a commonly used surface-characterization equipment is described. Arrangements have been made with a commercial publisher to produce a series of books, "Methods of Surface Characterization," which will address this need. Two Division staff members (Powell and Madey) and three other scientists (A. W. Czanderna at the Solar Energy Research Institute; D. M. Hercules and J. T. Yates at the University of Pittsburgh) constitute an editorial board that will oversee the production. A series of four volumes is currently planned which will describe the principles, techniques, and methods considered important for surface characterization. It is intended to describe how important surface-characterization measurements are made and how to ensure that the measurements and interpretations are satisfactory (to the greatest extent possible). The approach of the series will be pedagogical or tutorial.

Volumes 1 and 2 of the book series will describe the techniques and methods for electron spectroscopy and ion spectroscopy, respectively, which are in widespread use for surface analysis. These volumes will be concerned largely with techniques for which commercial instrumentation is available. It is hoped that writing for both volumes will be completed shortly.

Volume 3 will describe techniques for specimen handling and depth profiling. For specimen handling and treatment, this volume will provide a compilation of methods that have proven useful. This volume will also address the common artifacts and problems associated with the bombardment of solid surfaces by electrons and ions. Finally, a description will be given of methods for depth profiling. Preparation of this volume should be completed in 1986.

Volume 4 will bring together a description of methods for vibrational spectroscopy of molecules on surfaces. Most of the techniques are currently under active development; commercial instrumentation is available for some techniques but this situation could change in the next few years. The current state-of-the-art of each technique will be described as will the relative capabilities. An important component of the volume will be the summary of the relevant theory. This volume is essentially complete.

D. Standards-Committee Activities

Three staff members of the Division hold offices on two ASTM Committees, the E-42 Committee on Surface Analysis and the D-32 Committee on Catalysts, and on the recently established Surface Chemical Analysis Working Party organized under the auspices of the Versailles Project on Advanced Materials and Standards. Participation in the activities of these groups provides an opportunity for leadership, for dissemination of NBS expertise, and to learn of significant measurement problems in relevant areas.

1. ASTM Committee E-42 on Surface Analysis (C. J. Powell, J. Fine)

The ASTM Committee E-42 on Surface Analysis, founded in 1976, now has some 120 members; in addition, a large number of non-members, both within the U.S. and throughout the world, participate in Committee activities. The purpose of the Committee is to advance the field of surface analysis and the quality of surface analyses through the development of appropriate standards, standard practices, reference data, reference materials, round robins, symposia, workshops, and publications.

Committee activities of the past year have included development of the following documentary standards (which are at varying stages of approval):

- Additional definitions of terms for AES, XPS, SIMS, and Energetic Ion Analysis
- Guide to Depth Profiling in Auger Electron Spectroscopy
- Guide for Specimen Handling in AES and XPS
- Practice for Reporting Spectra in XPS
- Method for Calculating Data-Gathering Speed in XPS
- Guide to Steady-State Charge-Referencing Techniques in XPS
- Practice for Reporting Sputter Depth Profile Data in SIMS (secondary-ion mass spectroscopy)
- Guide to Determine the Depth Resolution in SIMS
- Guide for Specification of Ion Beams for Use in Surface Analysis
- Procedure for Sample Positioning with Cylindrical Mirror Analyzers in ISS (ion-scattering spectroscopy)
- Procedure for Approximate Energy Scale Calibration with Cylindrical Mirror Analyzers Used in ISS
- Proposed Guide for Data Reporting in ISS

The Standard Reference Data Subcommittee is conducting a survey of needs for reference data and of format requirements. A survey of the E-42 membership is being made to determine needs for new types of reference materials. Finally, a report has been submitted for publication recently of an ISS round robin involving comparisons of peak-position and peak-width measurements on a Cu-Ag-Au ternary alloy using seven cylindrical-mirror analyzers from the same manufacturer. This round robin showed that much of the spread in reported peak positions was associated with incorrect positioning of the specimen with respect to the analyzer.

The Committee has sponsored two symposia each year, one at the annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in the spring and the other at the National Symposium of the American Vacuum Society (AVS) in the fall. Papers presented at these symposia are published. After 1985, arrangements for the AVS Symposium will be made by the recently formed AVS Applied Surface Science Division. A workshop is held at each meeting to discuss particular measurement problems. At the 1984 AVS Symposium the topic was "Data Reduction for Quantification in Surface Analysis", and the topic at the 1985 Pittsburgh Conference was "Solving Industrial Problems with Surface Analysis".

The Committee is planning to prepare a booklet of E-42 surface analysis standards which will be published by ASTM. It is believed that many users of surface-analysis equipment will find the booklet to be a convenient compilation of terminology, guides, and recommended practices. The booklet will be updated roughly every two years and should be an effective means of disseminating E-42 standards.

2. Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS)
(C. J. Powell)

The "Versailles Agreement" arose from a meeting of the Heads of State or Government (Economic Summit) of industrialized nations at Versailles in 1982. The participants represented Canada, Federal Republic of Germany, France, Italy, Japan, United Kingdom, United States of America, and the Commission of the European Communities (CEC). A Summit Working Group on Technology, Growth, and Employment was established consisting of government science advisers. This group has established Working Groups in areas such as photovoltaic solar energy, food technology, advanced robotics, biotechnology, high speed trains, remote sensing from space, and advanced materials and standards. A summary of developments resulting from the Versailles Agreement was published as a News and Comment article recently in *Science* 228, 827 (1985).

The Versailles Project on Advanced Materials and Standards (VAMAS) consists of a Steering Committee with representatives from the seven nations above and the CEC. The overall aim of the project is to encourage international trade. This objective will result from international

agreement on codes of practice and performance standards and from multilateral research aimed at providing the scientific and technological base necessary to achieve agreement on standards. The project is essentially a scheme for stimulating the introduction of advanced materials into high technology products and engineering structures. The ubiquity of surface analysis through all sectors of high-technology industry has been demonstrated in recent surveys, and a proposal to establish a Surface Chemical Analysis (SCA) Working Party won early approval from the VAMAS Steering Committee. This SCA Working Party is now one of nine such groups that have been approved.

The main objective of the SCA working party is to produce, by coordinated effort, the reference procedures, data, and materials necessary to establish standards for surface chemical analysis. This effort is expected to lead to the international coordination of standards-related activities before national standards are adopted and to the development of standards on an international level.

National representatives to the SCA Working Party have been appointed with C. J. Powell as Chairman for a three-year period. The most urgent needs for surface analysis pertain to the use of Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and sputter-depth profiling (SDP). As projects in these areas become established and as other techniques come into greater use, it is expected that the project will broaden.

Qualitative and quantitative surface analyses require consideration of the following three items:

- (i) the physical principles of the measurement method;
- (ii) the behavior of the measuring instrument; and
- (iii) the interpretation and expression of the final result.

The basic principles of the physics of the various techniques and the selected analytical methods are vital since they lead to the working formulae which are used for quantitative analysis. Agreement must be obtained on these formulae and their regimes of applicability when working to certain accuracies for particular types of specimens and for particular techniques and methods. These formulae involve the measurement of intensities by the instrument which are then related to the composition at the surface by functions of the specimen material and the particular measurement process and by functions of the measuring instrument. Tabulations are needed of particular materials properties relevant to the various techniques and information is needed on instrument properties. Additionally, surface analyses can give chemical-state information, the interpretation of which requires a similar hierarchy of understanding, data, and reference procedures. The analyst therefore requires:

- (1) an agreed base of principles, definitions of terms, and equations to relate the techniques and procedures to the measurement;

- (2) reference procedures specifying how to measure intensities and spectral features;
- (3) reference procedures, reference data, and reference materials for calibrating instruments, determining instrument functions, and inter-relating instruments of different designs;
- (4) reference data of elemental sensitivity factors, matrix terms, information depths, libraries of chemical-state spectra, information on ion-sputtering rates, radiation damage, etc.; and
- (5) standard methods of specifying an analysis.

Details of specific needs for AES, XPS, SIMS, and SDP have been identified.

Suitable infrastructures have been developed in most VAMAS states for the SCA project. In the U.S., the ASTM Committee E-42 on Surface Analysis has agreed to participate and cooperate in VAMAS SCA projects. Standards already developed by the E-42 Committee will be disseminated to the other VAMAS states; standards developed later in the other states will be considered for adoption by the E-42 Committee. Suitable projects at NBS and other U.S. laboratories also contribute to the VAMAS SCA activity.

Since January, 1985, a large number of technical projects have been started in the VAMAS states, many largely as a result of the VAMAS initiative. These projects are largely national activities, as is to be expected since it is necessary that national needs, opportunities, and priorities be established prior to the development of more extensive bi-national or multi-national projects. The first meeting of the national representatives to the VAMAS SCA Working Party took place in October, 1985 during a conference in The Netherlands. A number of cooperative projects were discussed and it was agreed that the following should be implemented.

- (a) Development of thin oxide films as reference materials. It is planned to produce thin films of transition-metal oxides (Fe_2O_3 , NiO , and Cr_2O_3) with thicknesses of about 25 nm on metal substrates in Canada. Films of similar thickness of SiO_2 on silicon will be produced in Italy. These films will be characterized by sputter-depth profiling at a number of laboratories in Canada and Italy. The ion sputtering yields of these oxide films under common conditions of sputter-depth profiling will be compared with similar measurements on existing Ta_2O_5 and Ni/Cr reference materials at NPL and NBS.
- (b) Development of calibration data for the energy scales of Auger-electron spectrometers. Current projects exist at both NBS and NPL for the independent measurement of the kinetic energies of the principal Auger-electron transitions of copper, silver, and gold to be used as

calibration data in the energy range 50-2000 eV. After intercomparison, the calibration data will be utilized in an interlaboratory comparison of Auger-electron measurements to be organized by NPL.

- (c) Procedures for quantitative x-ray photoelectron spectroscopy (XPS). It is planned to investigate at NBS the suitability of recently fabricated Ta₂O₅ films on silicon and, if necessary, the oxide films prepared in project (a) as test materials for an interlaboratory comparison of angle-dependent XPS measurements. If these films can be cleaned adequately with minimal ion sputtering, NBS will organize the comparison of XPS measurements to give information on film thickness and film stoichiometry.

Two additional cooperative projects were discussed and it is likely that these will be initiated following the preparation of more definite plans. The first such project is the development of alumina reference materials with known concentrations of oxygen vacancies. These materials will be used as reference materials for problems in materials science such as wetting, adhesion, and electrical breakdown as well as for determining conditions for radiation damage. The second project is the development of reference procedures for high-resolution scanning Auger-electron microscopy so that the effects of topography, specimen crystallinity, and angle of emission can be minimized.

Plans are being developed for two workshops on surface chemical analysis for which VAMAS will be a co-sponsor. The first workshop is planned for October 24, 1986 at NBS and will precede the Tenth International Vacuum Congress and Sixth International Conference on Solid Surfaces to be held in Baltimore, October 27-31, 1986. The second workshop is planned for November 17, 1986 at NPL and will precede the fourth Conference on Quantitative Surface Analysis at NPL on November 18-20, 1986. These workshops will publicize VAMAS activities, disseminate results of recent work on quantitative surface analysis, and promote the development of new cooperative VAMAS projects. Specific attention will be given at both workshops to needs for reference data, needs for reference materials, methods of instrument calibration, and analytical methodology.

The VAMAS Surface Chemical Analysis Working Party has aroused a considerable amount of interest and enthusiasm in many of the VAMAS states. Many scientists believe that VAMAS has already provided and will continue to provide a considerable stimulus to the development of standards for surface chemical analysis in each state. Furthermore, through cooperation via VAMAS, national standards will be developed more efficiently and, it is hoped, without conflicts. The specific areas where international cooperation through VAMAS will be most effective are believed to be: (1) the development of data banks and preferred data formats; (2) the development of reference materials; (3) the development

of documentary standards for instrument operation and calibration; and (4) the development of recommended procedures for data acquisition, data reduction, and expression of final results.

3. ASTM Committee D-32 on Catalysts
(R. A. Haines and R. D. Kelley)

The activities of the ASTM Committee D-32 on Catalysts are concerned with the physical and chemical properties of commercial catalysts and with developing suitable procedures for catalytic activity measurements. The membership of the Committee numbers approximately 130. Semi-annual meetings are attended by between 60-90 percent of the membership which includes a significant international component. In the past year, the expansion of Committee activities has continued. These activities involve four sub-committees: Physical/Chemical Properties - 6 task groups; Physical/Mechanical Properties - 6 task groups; Chemical Analysis - 2 task groups; Catalytic Properties - 5 task groups. In general, this expansion has moved into areas that involve complex and often controversial measurements. Examples of these are the measurement of catalyst acidity, of the sensitivity of cracking catalysts to metallic impurities, and of multi-element chemical analysis by atomic absorption.

The Subcommittee on Chemical Analysis is chaired by R. D. Kelley. This Sub-Committee is involved in finishing the test method for analysis of platinum in fresh reforming catalysts. A "final" round robin is presently under way. The effort to analyze palladium in catalysts has progressed to the round robin stage. Standardization of x-ray fluorescence analytical procedures and of procedures for the chemical analysis of spent catalysts are being discussed. In the base-metals task group, the primary emphasis is on the development of a satisfactory test method for determining several base metals by optical atomic spectroscopy.

The NBS Office of Standard Reference Materials (OSRM) will soon distribute special reference materials for catalysts. As a member of D-32, Dr. Ruth Haines, Deputy Director of the Center for Chemical Physics, is preparing the documentation required for NBS acceptance of materials used by D-32 in various round robin tests. Five years ago the Committee recognized the need to preserve the catalysts, catalyst carriers and feed stock used in their round robins. D-32 sought a private sector distributor but none was found. The OSRM can distribute the materials at cost but NBS will not certify them. Initially, samples will be available for physical properties such as surface area and particle size distribution; mechanical properties such as crush strength; chemical analysis of supported metals; and reactivity via gas oil conversion microactivity tests. A series of zeolites will also be available for which diffraction intensity, unit cell dimensions and zeolite areas have been determined. All the materials should be available within the next six months. We can then judge the desirability of producing more standards based on the extent to which these samples are requested.

3. SURFACE MEASUREMENTS PROGRAM

C. Benndorf, D. R. Burgess, Jr., R. R. Cavanagh, A. Flodstrom,
J. W. Gadzuk, S. M. Girvin, T. J. Jach, R. D. Kelley, R. L. Kurtz,
T. E. Madey, D. E. Ramaker, N. D. Shinn, R. Stockbauer, P. D. Szuromi,
T J. Udovic, M. J. Wax

The Division undertakes a number of projects directed to the improved physical and chemical characterization of surfaces and surface processes. These projects meet Division objectives through the development of new measurement techniques, improvement of existing techniques, development of theories of the measurement process, applications to important scientific and national problems, development of measurement procedures, tests of the measurement system, development of new concepts, and provision of needed data.

A. Reaction Kinetics at High Pressures over Single Crystal Catalysts (P. D. Szuromi, M. J. Wax, T. J. Udovic, R. D. Kelley, T. E. Madey)

The overall objective of this research is to provide a molecular understanding of heterogeneous catalytic chemistry on well-characterized single-crystal surfaces. Among the areas studied are the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on metal surfaces, the mechanism of catalytic poisoning and promotion, and the reforming of alkanes over model supported Pt catalysts. The apparatus employed for these studies contains high pressure reactors contiguous to ultrahigh vacuum surface analysis chambers. The work is supported, in part, by the Division of Basic Energy Science of the Department of Energy.

Progress during the last year included studies of the hydrogenation activity of single-crystal W catalysts, as well as the poisoning effect of adsorbed S and the promoter effect of Pt thin films on the W substrates.

1. Ethane Hydrogenolysis Catalyzed by W(100)

Although W is not ordinarily considered a good catalyst, we have found that the W(100) surface is very effective in catalyzing ethane hydrogenolysis ($p \sim 100$ Torr, $550 < T < 620$ K). A carbidic overlayer forms rapidly in the early stages of reaction; this surface carbide is the "true" catalyst for the hydrogenolysis which proceeds with an activation energy of 27 kcal/mole. This is different from the activation energy for catalytic methanation over W(100), 14 kcal/mole, suggesting that methanation and hydrogenation do not share a rate-limiting step.

2. Thin Pt Films as Model Alkane Hydrogenolysis Catalysts

Vapor deposition of Pt onto a W(100) substrate in ultrahigh vacuum has been used to prepare model supported Pt catalysts which are free of extraneous promoters and poisons. Various Pt loadings (from fractional monolayer to multilayer) have been achieved reproducibly.

Although pure Pt is less active than W for ethane hydrogenolysis, the fractional monolayer Pt films catalyze hydrogenolysis at a rate significantly greater than the initially-clean W(100) surface.

3. Effect of S on Catalytic Methanation

The effect of adsorbed sulfur on the rate of catalytic methanation over a W(110) crystal has been studied as a function of sulfur coverage and crystal temperature. As in the case of the initially clean, non-sulfur-covered surface, carbidic carbon is formed during the course of the reaction. In Figure 3, the relative rate of reaction as a function of

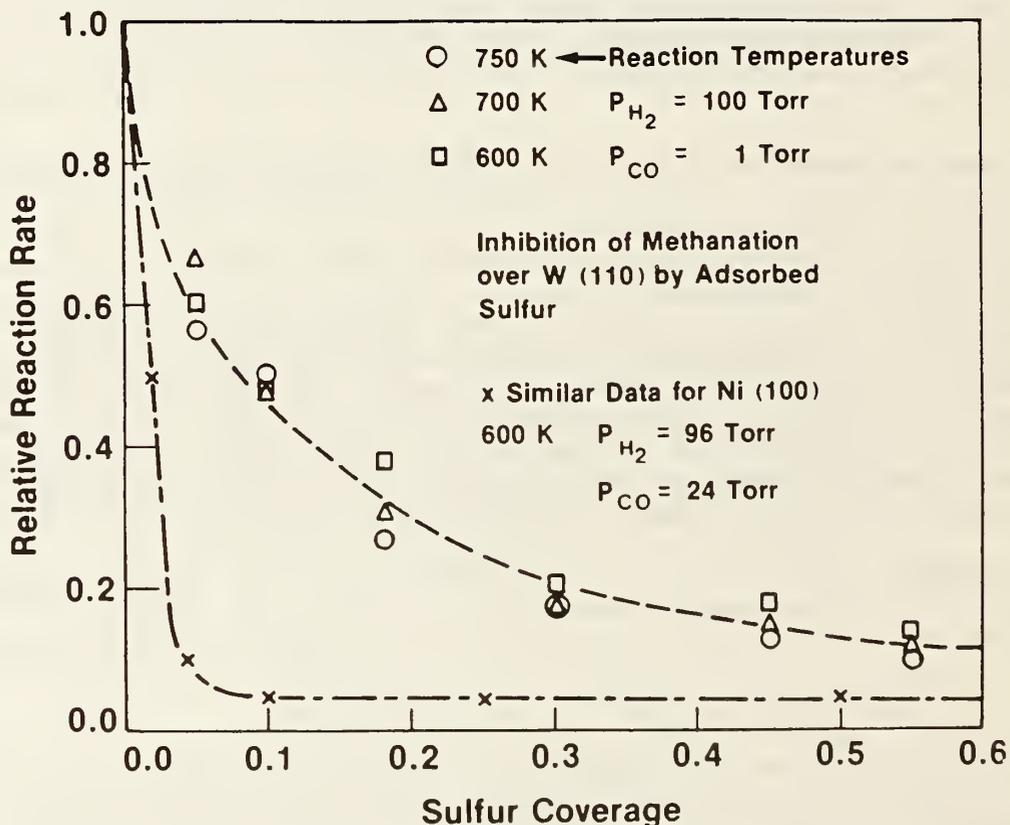


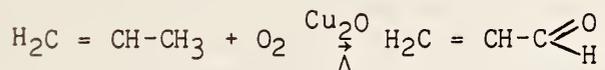
Fig. 3. Relative Reaction Rate for Catalytic Methanation over W(110) as a function of sulfur coverage (in fractions of a monolayer). Similar data for a Ni(100) are shown for comparison.

sulfur coverage (as determined by Auger-electron spectroscopy) is plotted for several reaction temperatures (together with similar data for Ni(100)). The Arrhenius energy of reaction, 56 kcal/mole, does not change substantially with sulfur coverage, as can be inferred from the similar inhibition of the rate of reaction for each temperature at a given coverage. Although the inhibition at low sulfur coverages is not as

dramatic as that seen previously for this reaction over nickel surfaces, the overall rate of reaction does drop about an order of magnitude at high coverages of sulfur.

We plan next year to complete both the methanation studies of W(110) and the effect of Pt films on hydrogenolysis. The role of Pt films in the thickness range 1-2 monolayers on W(100) will be characterized for the hydrogenolysis reaction.

We plan also to initiate a new project to study partial oxidation catalysts. This important class of reactions has received little attention from surface scientists, and we propose to probe the mechanism of the catalytic oxidation of propylene to acrolein over Cu_2O :



Initially, the dehydrogenation of alcohols will be examined on a pure copper crystal. These reactions will be examined using apparatus which combines both a high-pressure reactor (2 atmospheres) with an ultrahigh vacuum surface analysis chamber; the surface over which the catalytic reactions occur will be probed both before and after reaction. Several aspects of the oxidation reaction are not well understood: the effect of the surface geometry of the oxide; the electronic state of the catalyst, both the oxidation state of copper and the surface valence band structure; the influence of electronegative species (S, Se, halogens) as promoters; and the Arrhenius parameters for the overall rate of reaction. These questions can be addressed by employing: single-crystal oxide surfaces to control geometric effects; post-reaction analysis by electron spectroscopies (AES, XPS and UPS); preparation of clean surfaces in ultrahigh vacuum and of promoted samples of known surface concentration; and measurement of rate data over a wide range of temperatures, pressures and reactant ratios.

B. Molecular Structure and Reactivity on Surfaces as Studied Using ESDIAD and HREELS
(T. E. Madey, N. D. Shinn, and C. Benndorf)

A major challenge in surface science continues to be the determination of the structures of molecules on surfaces, particularly in the absence of long-range order. The goals of this project are to provide a direct determination of the structures of adsorbed molecules using the electron stimulated desorption ion angular distribution (ESDIAD) method, and to characterize the structures and reactivity of surface species using high resolution electron energy loss spectroscopy (HREELS). These techniques, both singly and in combination, are powerful tools for surface structural characterization.

The present thrusts of this project are (a) to determine the influence of surface additives (e.g., catalyst promoters and poisons) on the local structure and reactivity of small molecules (CO , NH_3 , H_2O) on

surfaces, and (b) to determine the structures of those molecules on initially-clean surfaces, particularly in controversial cases. The work has been supported in part by the Division of Basic Energy Sciences of the Department of Energy.

During the last year, progress has been made in the following areas.

1. Evidence for Reorientation of CO when co-adsorbed with K on Ru(001)

We have used ESDIAD to address a current controversy concerning the influence of K on the structure of adsorbed CO: does CO "stand up" or "lie down" adjacent to K on Ru(001)? In the absence of K, CO is bonded with its molecular axis perpendicular to Ru(001) at all coverages. Upon coadsorption with low coverages of K, ESDIAD measurements provide evidence for a strong local interaction between CO and K, which appears to result in a reorientation of the CO to an "inclined" or lying-down bonding configuration. Moreover, complementary thermal desorption and low-energy electron diffraction measurements suggest the formation of ordered surface species having $K_x(CO)_{2x}$ stoichiometry. The question of CO bonding geometry is a major area of current interest in the surface science community, and the present measurements and models provide new insights into the CO + K surface chemistry.

2. Structure and Reactivity of NH_3 on Clean and Modified Fe(100)

Iron is an excellent catalyst in NH_3 synthesis, and adsorbed K is known to "promote" the reaction by increasing the rate. In an attempt to understand at the molecular level how K influences the bonding geometry of NH_3 to Fe, we used ESDIAD to examine the structure and reactivity of NH_3 on clean Fe(100), and on K-dosed Fe(100). On clean Fe(100), adsorption of NH_3 occurs at step sites up to $\theta(NH_3) \sim 0.02$. For higher coverages, up to saturation of the first layer ($\theta(NH_3) \sim 0.34$), ESDIAD is dominated by a "halo" H^+ pattern indicating that NH_3 is bonded via the N atom and the H atoms (with no azimuthal ordering) are pointed away from the surface. The ESDIAD data correlate well with thermal desorption data, where different binding states due to fractional monolayer, second layer, and multilayer adsorption are observed. Only a small fraction ($\theta < 0.02$) of NH_3 dissociates upon heating. When NH_3 is coadsorbed with K, the ESDIAD and thermal desorption data indicate an interaction in which the NH_3 molecular axis is tilted and the binding energy to the substrate is decreased. In contrast, the interaction between NH_3 and O does not lead to structural changes or azimuthal ordering of NH_3 as reported previously on Ru(0001) and Ni(111) surfaces. This indicates that the $NH_3 - O$ distance is not optimal for attractive hydrogen bonding.

3. Structure of the Surface Hydration Shell of Bromide on Ag(110)

Surface science has been a valuable source of inspiration to electrochemists in recent years, particularly in studies of the interaction of water and other electrolytes with clean, well-characterized

electrode surfaces. In one such study, we have attempted to synthesize an electrochemical double layer in vacuum by examining the interaction of H₂O and bromine on an Ag(110) surface using ESDIAD, LEED (low-energy electron diffraction) and TDS (thermal desorption spectroscopy). Water adsorbed on clean Ag(110) formed a disordered, hydrogen-bonded overlayer. In the presence of adsorbed bromine, the adsorbed water was characterized by a higher binding energy and pronounced orientational order. The mixed adlayers resulting from this surface hydration of bromide also exhibited long range order. The surface hydration number ($n_{\text{H}_2\text{O}/\text{Br}}$) was two for $\theta_{\text{Br}} < 0.25$, and decreased to a few tenths at the Br saturation coverage, $\theta_{\text{Br}} = 0.75$. The present results have important implications for experiments in which investigators attempt to transfer electrodes from solution to a vacuum environment: neither water on the clean surface nor the hydration water remain adsorbed in vacuum at room temperature, and would be lost in a transfer experiment.

4. CO Chemisorption on Cr(110): Evidence for a Precursor to Dissociation

HREELS and ESDIAD studies of the chemisorption of CO on Cr(110) have provided fascinating insights into the structure and kinetics of molecular dissociation on a metal surface. At 120 K, two molecular binding modes of CO are sequentially populated. The first, $\alpha_1\text{CO}$, is a novel binding mode for a clean metal surface in which the molecules are bound with the C-O axis nearly parallel to the Cr(110) surface. Annealing experiments demonstrate that the α_1 binding mode is the precursor to dissociation on Cr(110). At higher CO coverages, $0.25 < \theta_{\text{CO}} < 0.35$, the $\alpha_1\text{CO}$ overlayer is disordered by the addition of the second binding mode, $\alpha_2\text{CO}$. The $\alpha_2\text{CO}$ species are terminally bound molecules adsorbed at a-top and bridge sites and aligned approximately perpendicular to the surface. Annealing studies of CO or O/CO adlayers provide evidence for a surface reaction in addition to direct dissociation at about 170 K. In contrast, adsorption at 300 K leads to direct dissociative chemisorption with no detectable intermediate molecular adsorbate. The implications of these results to catalytic reactions of CO have been considered and comparisons to CO adsorption on clean and "promoted" transition metal been made.

We plan next year to extend the ESDIAD method to the detection of negative ions; all ESDIAD measurements to date have involved positive ions. We believe that these challenging measurements will provide new insights into the structure and surface chemistry of a class of molecules (particularly those containing halogens and other electronegative groups) for which studies have not been possible previously. A new digital video system will be constructed for these measurements. This system will be used to acquire and process data for ion current versus emission angle. We expect that the digital system will be more sensitive and give more accurate information than the currently used analog system. A later phase of this work will involve characterization of similar molecules using

HREELS and synchrotron methods. The new measurements will be an exciting complement to our present studies of the influence of surface additives on the structure and chemistry of adsorbed species.

We will use ESDIAD and HREELS to address a fundamental question in hydrocarbon surface chemistry, namely, the structure of C_2H_2 on a Cu(110) surface. Different models have been proposed involving rehybridized carbon species with the C-C bond vector either parallel or perpendicular to the Cu atom rows. ESDIAD may be able to provide a unique insight into the local bonding geometry of this site.

Despite the extensive interest in the chemistry of H_2O on transition metal surfaces, there are no definitive spectroscopic studies of the adsorption and decomposition of H_2O in the temperature range 77-300K on any metal having a high heat of M-O bond formation where dissociation is likely to occur. We propose to study in detail the structure and kinetics of H_2O adsorption and decomposition on Cr(110) using ESDIAD and HREELS; the goal will be to identify the fundamental steps in this important surface reaction.

We will continue to probe the role of both electropositive and electronegative additives on the structure and chemistry of small adsorbed molecules. Of particular interest are the major differences in the "activity" of oxygen in promoting hydrogen abstraction on different surfaces.

C. Inelastic Neutron Scattering Studies of Adsorption and Reaction on Catalysts
(R. D. Kelley, R. R. Cavanagh, M. J. Wax, T. J. Udovic)

Inelastic incoherent neutron scattering (IINS) studies of adsorbates on catalyst surfaces are providing new insights into the vibrational spectroscopy of hydrogen and hydrogen-containing species adsorbed at the surfaces of high-area catalysts. NBS is ideally suited for these studies, having a unique combination of neutron physicists and surface chemists with an interest in catalysis. During the last year, advances have been made in characterization of both metal and zeolite catalysts using IINS at the NBS Reactor in collaboration with Dr. J. J. Rush of the Reactor Radiation Division. The work has been supported in part by the Division of Basic Energy Sciences of the Department of Energy.

1. Interaction of Vibrating H atoms on Pt particles

The dynamical interactions between vibrating hydrogen atoms on the surface of small Pt particles (Pt black) have been studied using IINS together with isotopic dilution (comparing pure H_{ads} with $H_{ads} + D_{ads}$). The data revealed direct information on the bonding state and dynamical non-bonded (as opposed to chemical) interactions of these species. Shifts and broadening of hydrogen vibrational features were accounted for in terms of mode dispersion due to strong H-H coupling.

2. Hydrogen Adsorption and Interaction with Oxygen on Pt

IINS was utilized to probe the nature of adsorbed hydrogen and its interaction with oxygen on platinum black. The vibrational spectra of adsorbed hydrogen at 80 K were found to be in agreement with the results of other reported IINS studies. The interaction of oxygen with adsorbed hydrogen provided vibrational spectra corroborating the existence of at least two distinct hydrogen-adsorption sites. In addition, hydrogen and oxygen adsorption on the platinum black blank both yielded spectral information concerning the chemical state of the platinum surface. Comparison of the present IINS data to published electron energy-loss spectroscopy results suggests that oxygen reacted with hydrogen over platinum black to product adsorbed hydroxyl (OH) species.

3. Neutron Scattering Study of Zeolite Rho

Incoherent inelastic neutron scattering has been used to examine the bonding of framework hydrogen to the faujasite zeolite rho in collaboration with Drs. G. D. Stucky, L. Abrams, and D. R. Corbin of Dupont. Vibrational spectra obtained from 160 to 1600 cm^{-1} are consistent with the existence of planar, symmetric AlO(H)Si units in the acid form of rho at room temperature. As the zeolite undergoes a slight change in structure on heating, an accompanying transfer of hydrogen atoms occurs to some new bonding site of unknown nature which is characterized by an unusually large-amplitude, low-energy vibration. Quasielastic neutron scattering data have allowed an upper limit ($4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 673 K) to be set for the rate of diffusion of hydrogen on the framework of partially dehydroxylated rho, a result consistent with diffusion measurements by macroscopic methods.

We plan next year to extend the applications of IINS to the characterization of adsorbates on the internal and external surfaces of zeolite catalysts. The new measurements will build upon our recent studies of the bonding and of diffusion rates of framework hydrogen of zeolite rho, and will include both adsorbate structures and diffusive motion of adsorbates in various zeolites. One example will be the dynamics of NH_3 interactions in zeolite rho. Quasielastic neutron scattering will complement the IINS measurements, and will be used to derive the rates and nature of diffusional motion.

We will use IINS to probe the interactions of hydrogen on and in Pd black. The main effort will be devoted to cleaning and characterizing the sample before hydrogen adsorption, followed by a study of both surface and bulk hydrogen in Pd. This effort is expected to answer long-standing questions regarding the communication between surface and bulk species.

There have been few studies of adsorption and reactions on supported catalysts using IINS. Our studies to date have involved the adsorption of H_2 and small hydrocarbons on unsupported metals (Ni, Pt). We plan to extend these studies to supported metal catalysts for which there is a vast literature concerning preparation, cleaning, adsorption and reaction. In

collaboration with workers experienced in noble-metal catalyst preparation, we will choose, prepare and initiate neutron-scattering studies on prototype catalysts.

D. Surface Characterization Using Synchrotron Radiation

(R. Stockbauer, R. L. Kurtz, N. D. Shinn, D. E. Ramaker, A. Flodstrom, and T. E. Madey)

Major goals of this effort are (a) to determine the electronic structure of surfaces and adsorbates using variable-wavelength synchrotron radiation and ultraviolet photoelectron spectroscopy (UPS), and (b) to identify the electronic excitations which result in the photon-stimulated desorption (PSD) of ions from molecules adsorbed on surfaces as well as from condensed molecular films. When possible, PSD ion yields are correlated with UPS of both valence states and core-electronic states of the surface species. These measurements provide tests of recent theoretical models of electron- and photon-stimulated desorption, and provide new insights into the bond-breaking processes induced by ionizing radiation incident on surfaces. The work has been supported in part by the Office of Naval Research.

Accomplishments during the past year were in six areas:

(1) electronic structure of molecules adsorbed on surfaces; (2) electron-stimulated desorption (ESD) and PSD of oxide surfaces; (3) instrumentation of a new beamline at the NBS synchrotron radiation facility SURF-II; (4) construction of a new display analyzer; (5) progress at the Brookhaven National Synchrotron Light Source (NSLS); and (6) theory of stimulated desorption.

1. Electronic Structure of Molecules Adsorbed on Surfaces: Relation to Geometric Structure

Synchrotron photoemission studies of the bonding of CO to the Cr(110) surface at low temperatures have identified differences in the electronic structure of the molecularly adsorbed CO that are correlated to the molecular binding configuration. At low coverages ($\theta < 0.25$), only the α_1 CO binding state is populated; in this binding state the molecules are "lying down" on the metal surface. Ultraviolet photoemission measurements reveal a unique Cr:CO 4σ bonding interaction; this result is evidence for Cr:CO bonding substantially different from the conventional Blyholder model of synergistic CO $5\sigma \rightarrow$ metal charge donation and metal \rightarrow CO 1π backdonation. In contrast, the terminally-bonded α_2 CO binding mode, seen at high surface coverage ($\theta > 0.25$), is well described by this conventional model.

Figure 4 illustrates typical UPS data obtained at 40 eV photon energy in an experimental configuration which is most sensitive to photoelectron detection along the [110] surface normal direction. A spectrum for the clean Cr(110) surface, Figure 4(a), can be compared to those with only α_1 CO adsorbed, Figure 4(b), and with both α_1 CO and α_2 CO adsorbed at high coverage, Figure 4(c). The spectral differences associated with the two

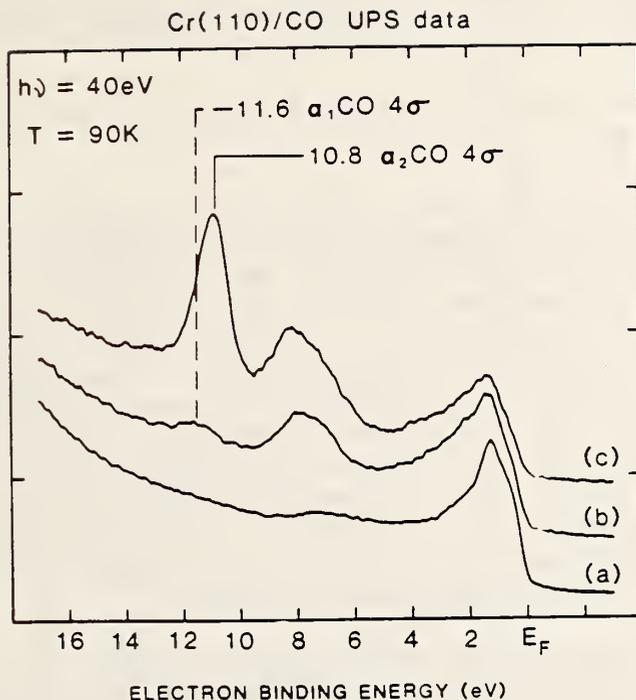


Fig. 4. Ultraviolet photoemission spectroscopy (UPS) data for CO on a Cr(110) surface; evidence for two different bonding configurations are presented. Curve (a) is the clean surface spectrum and curve (b) corresponds to the α_1 state of CO (the "lying-down" mode). Curve (c) is the spectrum which includes the α_2 state of CO (the "standing-up" mode).

binding modes are unmistakable; a weak $\alpha_1\text{CO } 4\sigma$ peak at 11.6 eV binding energy is seen in Figure 4(b) whereas an intense $\alpha_2\text{CO } 4\sigma$ peak at 10.8 eV is observed in Figure 4(c). Both the binding energy and intensity differences are strong evidence for the radically different CO binding geometries and resulting bonding variations.

Angular and photon-energy dependent data provide additional support for the CO-binding mode models developed from our previous HREELS/ESDIAD studies (Section 3.B.4). Further studies probing the dissociation of adsorbed CO and CO:O₂ interactions on Cr(110) have been performed. As first seen in the earlier vibrational studies, adsorbate interactions between co-adsorbed CO and oxygen result in the reorientation of the lying-down carbon monoxide to a terminally-bonded configuration; this mode conversion is manifested in the UPS data by the expected changes in the CO 4σ region of the spectra.

Preliminary data have been obtained for molecular nitrogen, an isoelectronic non-polar analog to CO, adsorbed on the Cr(110) surface. These results will be combined with subsequent vibrational data to determine whether a molecular "lying down" $N_2(\text{ads})$ species, analogous to $\alpha_1\text{CO}$, is present.

2. Electron and Photon-Stimulated Desorption of Ions from Oxide Surfaces

As part of our continuing effort to understand the mechanisms involved in stimulated desorption of ions from surfaces, we have made measurements on single-crystal oxides that have forced a re-evaluation of currently accepted theories. Much of the previous work in stimulated desorption involves correlation of photon energies for producing desorption with photon spectroscopic data for atomic excitations. Such work originally gave rise to fundamentally new ideas about the types of atomic transitions that could produce desorbing ions. These mechanisms, however, are incomplete in several aspects and in particular they neglect the influence of local bonding geometries and surface structure. The experimental program presently underway is aimed at studying the influence of surface structure and is giving rise to a broader understanding of the mechanisms underlying the desorption process.

The surfaces studied to date include the (001) and (110) surfaces of TiO_2 . This material is particularly important since it is the model system for the Knotek-Feibelman (KF) mechanism of desorption. This model describes the inter-atomic Auger process that can occur in a maximal-valent material such as TiO_2 when a core hole is produced in the cation by electron or photon impact. This hole is unstable and can decay by an inter-atomic Auger process involving charge transfer from the O^{2-} ligands. This results in a positively charged O-ligand which then desorbs due to the strongly repulsive Madelung potential. This model predicts that excitation of the Ti 3p level should produce desorption. It also predicts that any population of Ti 3d-electron states (i.e. no longer a maximal-valent surface) should strongly reduce the probability of the inter-atomic decay, favoring an intra-atomic decay. This would result in a much reduced ion yield.

Figure 5(b) shows the oxygen ion yield versus incident photon energy from a 700°C annealed $\text{TiO}_2(001)$ surface; this is a maximal-valent surface. At the excitation energy of the Ti 3p level, 38 eV, there is an onset in the ion yield. It peaks at 47 eV and decays rapidly, following the decay of the excitation probability of the Ti 3p level. In Figure 5(a), we show the 0 eV constant-final-state spectrum, essentially the photoabsorption spectrum of this surface. By comparison of this and other electron-excitation spectra with the ion emission spectra, we hope to unravel the specifics of the electronic excitations that product desorption. Thus, in agreement with the predictions of the KF mechanism, we observe desorption due to the excitation of the Ti 3p level. This agreement ends, however, when we compare the magnitudes of these yield curves for the different surfaces studied.

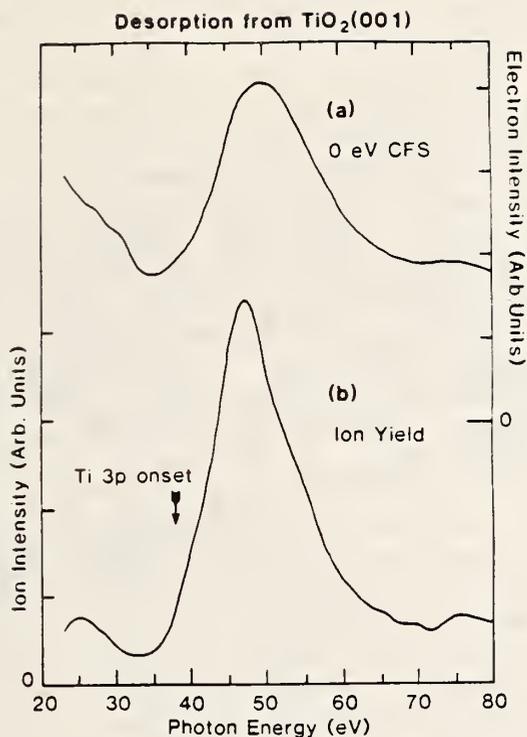


Fig. 5. Photon-stimulated desorption (PSD) of oxygen ions from an annealed TiO₂ (001) surface showing the role of core-hole excitations. (a) 0 eV constant-final-state intensity (proportional to photoabsorption cross section) versus photon energy. (b) ion yield versus photon energy.

The unexpected behavior that we have observed occurs when surface species are intentionally made non-maximal-valent (Ti 3d-electron states now populated) by the introduction of defects (by 500 eV Ar⁺-ion bombardment); the magnitude of the ion yield does not always decrease as the KF mechanism would predict. It has been observed that the ion yield can even increase with such treatment, the opposite of the behavior that would be predicted by the KF mechanism. The source of this conflict can be resolved, however, when one considers the influence of surface structure and the local site geometries on the process.

It is known that surface geometric structure is drastically modified by Ar⁺-ion bombardment; however, the details of the atomic rearrangements that the bombardment produces are not known. In order to compare the ion emission from surfaces with different geometries, we have resorted to

studying two different surfaces of TiO_2 , namely the (001) and the (110). The (001) surface is known to facet on annealing to (011) planes while the (110) surface is flat. The electron stimulated desorption ion angular distributions (ESDIAD) that we observe from the (001) surface are consistent with such a faceting; we observe emission from the faces and the edges of facets. The ESDIAD patterns from the (110) surface, on the other hand, give only a normal emission spot. Comparison of the magnitudes of the ion yields from these surfaces, however, indicates that increased ligand coordination of the Ti cations (such as is expected to be the case for a flat surface) produces decreased probability of ion desorption. The origin of this decreased probability could be an enhanced reneutralization probability or a decrease in the probability of initial excitation. There is also the possibility that surface dynamics may strongly influence the ion escape by lattice polarization and recapture. Our interest in the relative influences of these additional processes in desorption is to understand not only the initial excitation but also the decay of this excitation and the subsequent surface dynamics that lead to ion and neutral desorption.

In order to better understand the structure of complicated surfaces such as those of TiO_2 , a graphics package has been written in FORTRAN that allows the display of ball-model crystal surfaces. This routine allows one to define a basis for a lattice, create a bulk crystal of specified size, and cut planes through this crystal to expose arbitrary surfaces. These surfaces can be rotated to be viewed from any perspective and surface vacancies can be introduced interactively. One such crystal ball model is shown in Figure 6 where the facet believed to be formed on $\text{TiO}_2(001)$ after annealing to 700°C is shown. This modeling of surface structures will be associated with planned molecular dynamics calculations to be done in conjunction with our experimental efforts; we hope to better understand the variety of processes that influence desorption. Such calculations could allow us to predict site-specific desorption probabilities and to model desorption trajectories (perhaps even predict ESDIAD patterns). It is expected that such a feedback between calculation and experiment will also result in a better understanding of the structure of both perfect and defective surfaces.

During the next year, we plan to continue to study the mechanisms of ion desorption from solid oxide surfaces with both experimental studies and model calculations. Oxides have been shown to be unique systems that allow investigation of the relation between desorption mechanisms and the electronic and geometric structure. We will investigate further desorption from various surfaces of TiO_2 . The recent studies of desorption from the (001) and the (110) surfaces of TiO_2 have promoted interest in the comparative study of $\text{TiO}_2(011)$ and $\text{Ti}_2\text{O}_3(1012)$. Their similar surface geometric structures should permit isolation of the influence of their different electronic structures on the core-hole decay processes that lead to desorption. In addition, we intend to investigate the influence of the local-site environment in ion desorption from other surface such as $\text{MgO}(100)$ and faceted MgO .

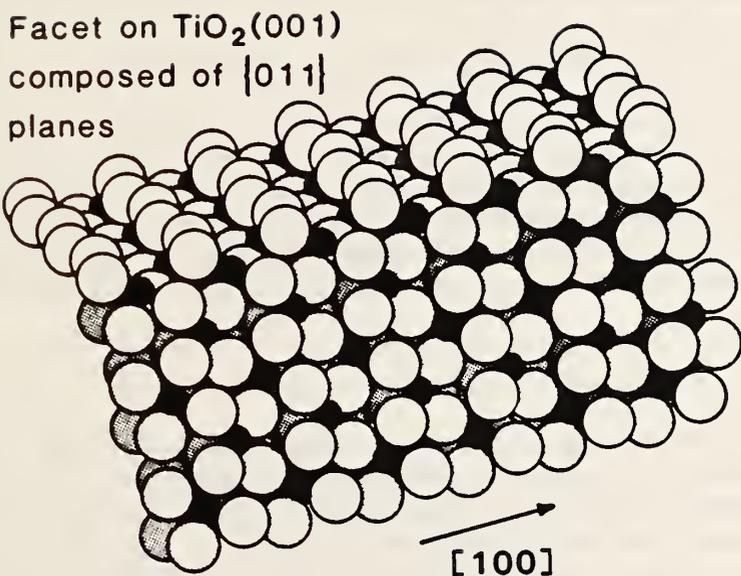


Fig. 6. Computer-generated model of faceted $\text{TiO}_2(001)$ surface.

We plan to make a molecular-dynamics calculation of the lattice response to a desorption process. An investigation will first be made of the often complicated geometric structure of oxide surfaces using software that can produce ball-model drawings of idealized surfaces. This software will be combined with the molecular-dynamics calculation in which the initial excitation and decay are assumed to occur rapidly; the subsequent charge reversal of a ligand then results in the motion of both the ligand and the rest of the lattice. The calculation should reveal information about the specifics of the sites that result in desorption and their angular distributions.

3. New Beam Line at SURF-II

The Surface Science Division has established a new beam line at the NBS synchrotron light source SURF-II. This will replace the existing beam line which we have used for the past 5 years. The heart of the new beam line is a toroidal grating monochromator designed by us to deliver high photon flux to investigate ion emission from surfaces with low ion yield. The monochromator has been calibrated and characterized and delivers 1×10^{10} photons per second per milliamp of ring current at a wavelength resolution of 4 Å. With SURF-II routinely operating in the

100 mA range, we will have $\sim 10^{12}$ photons per second on the sample at the same resolution. The useful energy range is from 17 to 90 eV. A new laminar grating is being manufactured which will decrease the amount of second order light being transmitted, and a second new grating will extend the range of the monochromator to 180 eV.

4. Construction of Angle-Resolving Display Analyzer

A new ellipsoidal-mirror angle-resolving electron- and ion-energy analyzer is nearing completion. This outstanding instrument was designed at NBS (based on an instrument constructed at IBM by D. Eastman) and is being constructed here. It is ideally suited for angle-resolved PSD, and will be the only such analyzer in North America used for the measurements. Details and scientific plans are given in Section 4.B.3.

5. Experiments at the Brookhaven National Synchrotron Light Source

A major effort during the last several years has been the initiation of an NBS-Naval Research Laboratory collaboration to establish four beamlines at the Brookhaven National Synchrotron Light Source (NSLS). We are providing surface science instrumentation to be used on one of the beamlines at the x-ray ring. The planned experiments have been delayed due to machine problems but these now appear to be largely overcome.

Our planned research will be an extension of the experiments performed at the NBS SURF-II facility (see above) to the higher-photon energies and more intense light available at the NSLS. Light from a unique, extended-range monochromator (5-5000 eV) will be used to study surface electronic structure and surface bonding of molecules. Experimental probes will include photoemission spectroscopy, surface extended x-ray absorption fine structure, and photon-stimulated desorption.

The main experimental chamber has been installed at NSLS and a sample preparation chamber has been acquired. The first experiments using the limited range of the monochromator presently available (20-200 eV) will involve measurements of electron attenuation lengths as a function of electron kinetic energy for condensed thin films of molecular solids. The synchrotron-based method for these measurements was developed and tested at SURF-II. These measurements will provide benchmark data for electron transport through organic materials in an energy range near the minimum value of the attenuation length. When the monochromator energy range is extended to ~ 1000 eV, we will undertake detailed studies of the roles of both core-level and valence excitation in the photon-stimulated desorption of ions from covalently bonded molecules on surface.

6. Theory of Stimulated Desorption

Work continued on the elucidation of the mechanisms that can give rise to electron- and photon-stimulated desorption of ions from adsorbates on surfaces as well as from single crystals. During this year, attention was given to the role of secondary electrons in photon-stimulated desorption and the extent to which these effects distort the ion yield spectra. Our studies suggest that these effects are not as dramatic as indicated in the literature. Work was also begun on understanding the mechanisms for negative-ion desorption from surfaces under electron bombardment and the role these mechanisms may play in negative-ion ESDIAD. Our understanding of the role of secondary electrons and the mechanisms for negative-ion desorption are important for planned future experiments (Section 3.B).

E. Dynamical Effects Associated with Core-Level Ionization (T. J. Jach)

The NBS Quantum Metrology Group under the direction of Dr. R. D. Deslattes is developing an experiment to study electronic effects associated with core-level ionization in atoms, molecules, and at surfaces. Specific effects to be studied include dynamical effects in inner-shell vacancy production, relaxation of the extra-atomic environment, and production of multiple vacancies with or without ionization. One member of the Surface Science Division staff has been assigned to work half-time on this project.

During the past year, experimental work involving synchrotron radiation was pursued with two particular goals in mind. First, the long-awaited routine operation of the x-ray ring of the Brookhaven National Synchrotron Light Source (NSLS) became a reality. We aligned and corrected problems in our tunable focussed soft x-ray beamline (X-24A) to the point where it is the most intense source of photons in the 2-7 keV photons available in the world ($\sim 10^{11}$ photons/sec at 3 keV with < 0.4 eV resolution). Second, we initiated experiments to study multi-electron core-level excitations in atoms and at surfaces.

1. NSLS X-24A Soft X-Ray Beamline (800 eV-7 keV)

The development of the NSLS X-24A beamline at Brookhaven officially came to fruition in September with the production of a stable, focussed, tunable x-ray beam in the energy range 2-7 keV. Using a nickel-coated aluminum collecting mirror (which also acts as a low-pass filter), a double-crystal monochromator, and a nickel-coated focussing mirror, we obtained a focussed spot 2 mm high by 1 mm wide with the flux mentioned above. The entire system is in ultra-high vacuum (uhv) with no windows whatsoever (it is contiguous with the main ring vacuum) and operates stably and comfortably at the highest intensity conditions reached by the x-ray ring so far (125 mA stored current at 2.5 GeV). The system is entirely computer controlled. The flux at this time exceeds all other tuned sources including the LBL/Exxon 54-pole wiggler at the Stanford

Synchrotron Research Laboratory over the energy range described above. Although an active program of experiments has already begun, we are actively soliciting other potential users.

2. Photon-Excited Multi-Electron Core-Level Excitations Using Synchrotron Radiation

We have begun a series of experiments aimed at the better understanding of multi-electron excitations which are photoexcited. Such effects as the threshold behavior of x-ray resonant Raman fluorescence, the energy shift due to post-collisional interactions, and the couplings between different decay channels from multi-electron excited states are all topics of importance in a number of surface spectroscopies. In collaboration with the NBS Quantum Metrology Group, we have initiated a three-step program: first, to observe x-ray fluorescence and Auger-electron decay in monatomic gases; second, to observe these decays in multi-atom gases; and finally, to observe the decays from solid surfaces of transition metals. All of these measurements are to be made as a function of photon energy in the vicinity of the threshold energies for core-level ionization. Data such as line widths, energy shifts, and threshold behavior will be used to understand multi-electron excited states and the dynamics of the decay process.

During the past year we have taken preliminary data on two systems. We observed K-shell x-ray fluorescence from argon gas using a windowed gas cell and a uhv bent-crystal (Si) x-ray spectrometer. This work was the first experiment on the x-24A beamline at NSLS described above. The incorporation of ion chambers into the gas cell allowed us to tune precisely the incident beam energy anywhere in the vicinity of the argon K-edge (including the 4p "white line") and permitted precise tuning of both the input and output photons.

The second system used an argon gas jet in vacuum and a cylindrical-mirror electron energy analyzer to observe K-shell photoemission and KVV Auger-electron decay. This system was put into operation on the 54-pole wiggler beam line at the Stanford Synchrotron Research Laboratory. The wiggler was operated as an undulator for the first time and once again ion chambers monitoring absorption of the photons in argon gas were used to tune the incident beam.

Both experimental systems yielded spectra with count rates lower than expected. The coming year will be devoted to system modifications which are intended to give higher count rates and eliminate other problems which showed up in the first runs. The same systems will, of course, be used to take data on monatomic and more complex gases.

A surface-science chamber which has been designed to perform uhv studies on the x-24A beamline or elsewhere is presently being constructed. It will permit us to perform the second phase of the multi-electron excitation work using thin films and single crystals of transition metals. The lower energy limit of this beamline (~800 eV) was intentionally chosen

to allow study of the L-shell excitations in nickel and copper. We have previously studied the Auger-electron spectra of these metals with near-threshold electron excitation and believe that experiments with near-threshold photon excitation will help resolve uncertainties in interpretation. We expect to measure x-ray fluorescence, photoemission, and Auger-electron spectra in the new experiments. Our new chamber will incorporate a precision goniometer, allowing added surface sensitivity to be obtained by orienting the sample at glancing incidence.

F. Production and Characterization of Ultrasmooth Surfaces
(T. J. Jach)

Previous surface science experiments have indicated a need for surfaces which are extremely flat and smooth on an atomic scale. An example of this need is the desire to study photoemission from a metallic thin film at grazing incidence to obtain maximum surface sensitivity. There are also obvious reasons for wanting to make smooth defect-free substrates and thin films such as in the semiconductor industry where device widths of 100Å are being approached. We have initiated an effort to (a) characterize substrates and thin films for roughness down to a scale of 3Å; and (b) push the limit of surface smoothness attainable to 10Å or better for a variety of materials.

Reflection electron microscopy (REM) has been used to measure the roughness of metal surfaces. In collaboration with Drs. G. Hembree of the NBS Mechanical Production Metrology Division and L. B. Holdeman of Comsat, a series of thin gold films were deposited on float glass substrates at a range of temperatures between 30°C to 430°C. We have been able to photograph structure on the film surfaces with a resolution of about 10Å. The study indicated that gold films deposited at room temperature are far rougher (100Å rms or greater) than previously thought; other standard techniques such as stylus or scanning electron microscopy photos failed to reveal this roughness. REM should be capable of directly detecting step dislocations or other such features on gold films down to a height of one atom; such a resolution is almost as good as scanning tunneling microscopy. The methods are complementary, however, since REM is better at looking at large areas rather than small ones. We have also determined that the roughness is due to initial surface nucleation and whisker growth which varies in a complex way with temperature.

During the following year, we will be extending the reflection electron microscopy technique to examine GaAs substrates as well as continuing work on the gold films. We hope that the success we have had in characterizing gold films can be used to determine the polishing and etching methods that produce the smoothest GaAs substrates.

G. Laser Diagnostics of Surface Dynamics
(D. R. Burgess, Jr. and R. R. Cavanagh)

The pathways and rates of energy transfer at surfaces remain the key unresolved issues for understanding chemical reactions at interfaces. Such information has eluded experiments which rely on conventional surface-characterization techniques. A variety of laser-based techniques, however, have recently demonstrated their utility in probing such molecular dynamics in both the gaseous and liquid states. In this program, the focus is on exploiting similar laser-based techniques for addressing the issues of energy transfer at surfaces. The program utilizes both the temporal and spectral characteristics available in state-of-the-art lasers. Strong collaborations with Drs. M. P. Casassa, E. J. Heilweil, D. S. King, D. A. Mantell and J. C. Stephenson of the NBS Molecular Spectroscopy Division play a vital role in these efforts.

1. Laser-Excited Fluorescence as a Probe of the Dynamics of Thermal Desorption

Thermally activated desorption remains a key step in a wide variety of reactions at surfaces. While it is frequently assumed that the desorbed species can be accurately viewed as being in equilibrium with the surface, there have been no direct tests of this assumption. For instance, the potential for developing surface chemistries which exploit non-equilibrium reactions of excited-state species will depend on the efficiency of the accommodation process.

We have studied the thermal desorption of NO from Pt(111) using laser-excited fluorescence. The rotational-state distribution have been examined as a function of NO coverage ($\theta = 0.1$ to 1.0 of saturation) and we have found that the internal energy of the desorbed NO can be described by a Boltzmann distribution with $T_{\text{int}} = (0.95 \pm 0.05) T_{\text{surf}}$ (see Figure 7). We have also examined the influence of coadsorbed CO. While the adsorption sequence can change the desorption rate of the NO, resulting in temperatures for the maximum desorption rate being lowered by 25%, the internal energy is still found to be distributed in a Boltzmann manner, with $T_{\text{int}} \approx T_{\text{surf}}$. Additional experiments to probe the extent of rotational alignment of the desorbed NO have indicated that there is no preferred spatial orientation of the rotational angular momentum. Experiments to measure the kinetic energy in individual rotational states are presently in progress. It is anticipated that the degree of accommodation found for the NO/Pt(111) system will make it an excellent "benchmark" in future studies of rapid desorption processes (see Sections 2 and 4 below). Future plans include the extension of the NO/Pt(111) measurements to the NO/Pt(110) system in order to probe the influence of competition from step-induced NO dissociation with the molecular NO desorption channel. This work is supported in part by the Department of Energy.

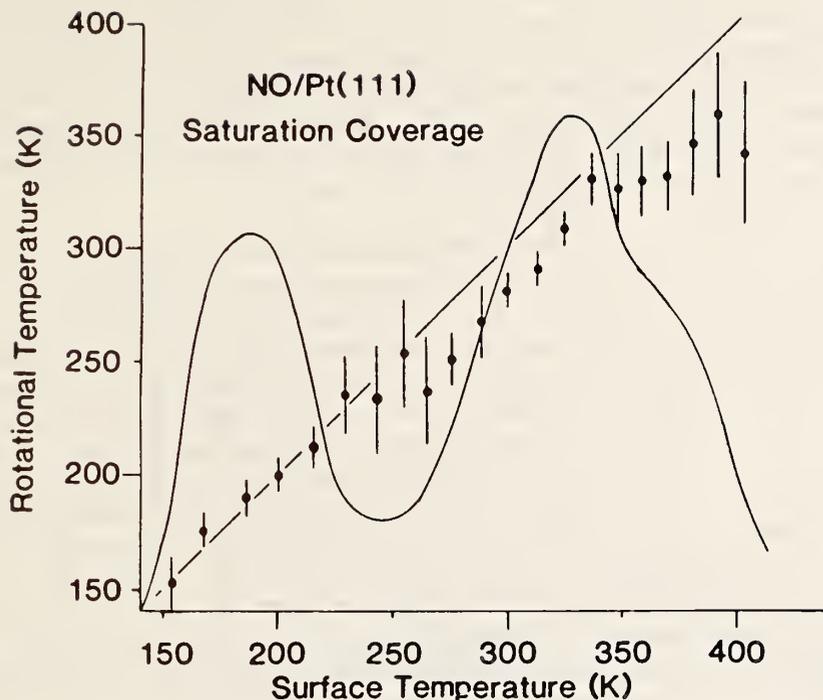


Fig. 7. Rotational temperature of NO thermally desorbed from Pt(111), determined by laser-excited fluorescence, as a function of surface temperature.

2. Laser-Induced Desorption

Lasers have recently become popular tools for inducing desorption from surfaces. The majority of the work in this area has focused on the removal of near-monolayer quantities of adsorbed species within the region illuminated by the laser. From the gas-phase species which are generated, one can identify and measure concentration gradients of adsorbates and probe adsorbate diffusion by monitoring the relaxation of the laser-induced concentration gradient. We have recently begun a series of experiments aimed at using laser-excited fluorescence to measure the internal-energy distribution as a result of desorption induced by a laser pulse.

In the past year we have been able to assemble a vacuum system for these studies. It is anticipated that this system will permit us to use laser-excited fluorescence and multi-photon ionization as state-specific probes of the laser-induced desorption process. We have already successfully used a quadrupole mass spectrometer to probe the desorption of H₂, CO, and NO from a polycrystalline platinum foil upon irradiation with the second harmonic from a frequency-doubled NdYAG laser. The laser-

desorption yield has been monitored both as a function of the surface-temperature rise (laser pulse energy) and as a function of surface coverage. In all cases, the desorption yield was non-linear in laser intensity and there was a minimum energy density below which no detectable desorption was observed. Furthermore, this threshold decreased with increasing coverage, consistent with the shift to lower temperatures observed in standard thermal desorption experiments.

A major concern in all experiments where a laser is used to heat a surface is the accurate determination of the surface temperature. Classical heat conduction equations have been employed to establish the surface temperature in the past, and are currently being used to analyze the desorption yields obtained in this laboratory. However, experimental efforts to validate the surface temperature actually achieved due to laser heating are sparse. A direct measure of the laser perturbation of the surface properties would offer the most satisfactory probe of the heating effects. At this time we are examining the utility of blackbody radiation as a signature of the extent and the reproducibility of laser-surface heating. It is anticipated that state-specific detection will be incorporated into this experiment in the coming year in order to determine the degree to which laser heating is manifest in the internal and translational energies of the desorbed molecules. This work is supported in part by the Department of Energy.

3. Time resolved measurements of vibrational energy transfer

Direct characterization of the time scales and mechanisms for relaxation and dephasing of vibrational excitation in adsorbed layers is the aim of this work. Such measurements can provide a quantitative understanding of a substrate's ability to quench the energy released upon chemisorption, reaction, or irradiation.

Following our report last year of the first measurements of vibrational relaxation on surfaces (OH on colloidal SiO_2), the technique has been extended to self-supporting pressed discs of the same material. A longer T_1 time for population decay was observed (220 ± 20 ps) than in any of the measurements where a solvent was also present. Chemical treatment of the SiO_2 surfaces has generated BOH, NH_2 , and OCH_3 adsorbates which have been probed. The temperature dependence of the vibrational relaxation rate for both OH and OD on SiO_2 has been measured and each is found to fit a multiphonon model for the thermally-enhanced relaxation (see Figure 8). These experiments provide a first test of the pathways involved in vibrational relaxation at surfaces. They also demonstrate that over the temperature range employed by most industrial reactors, the relaxation mechanisms on this model catalytic support can be generally accounted for by a simple multiphonon model of the relaxation process. Additional work has extended the technique to relaxation measurements of the OH groups on the zeolite ZSM-5 and of both OH groups and free carriers on ZnO.

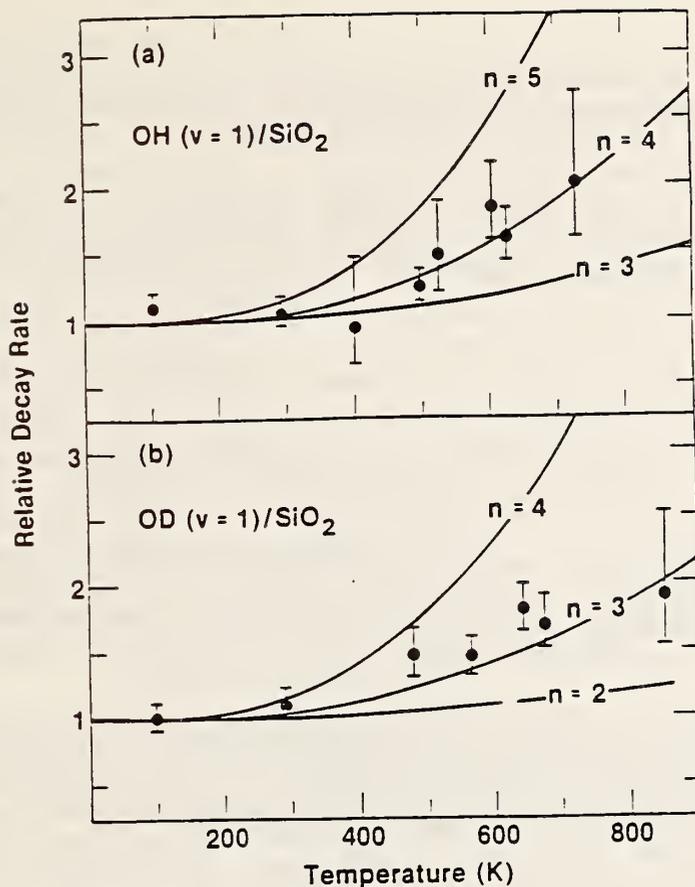


Fig. 8. Vibrational relaxation rates ($1/T_1$) for OH and OD as a function of temperature. For each isotope, the rates have been normalized to the rates observed at room temperature. The solid curves represent the temperature dependence of the relaxation rate predicted by a multiphonon relaxation model, where n is the number of phonons involved in the relaxation process.

Future work is planned on a range of zeolites in an effort to measure the differences between the vibrational relaxation rates for OH groups bound at silica sites as compared to alumina sites. It has long been postulated that these two sites have distinctly different catalytic activity and thus it is reasonable to expect that they will have distinctly different vibrational relaxation rates. By comparing a range of samples with known catalytic activity, it will be possible to ascertain the degree of correlation between the observed relaxation rates and the catalytic activity. We also anticipate that the existing laser system can be extended into the absorption range of the adsorbed carbon monoxide fundamental. With this advance in picosecond laser technology, we will be able to explore the T_1 times for CO bound to small supported transition-metal particles. This project is supported in part by the Air Force Office of Scientific Research.

4. High-Resolution Infrared Reflection-Absorption Spectroscopy and Picosecond/Femtosecond Measurements

To date, we have been able to contribute to a more detailed picture of the relevant steps in energy transfer at surfaces. While there remains a great deal still to be done with the techniques which we have developed, it is becoming clear that several major advances will be required before direct measurements of vibrational relaxation at well-characterized single-crystal surfaces will be possible. The four major technical issues which must be addressed are: i) Extension of the tuning range down to 5 μm in order to probe oscillators with large absorption cross sections such as CO and NO. ii) Increased time resolution to the range of ≤ 2 ps in order to follow the faster relaxation rates anticipated for systems which can couple to electron-hole pairs. iii) A high-resolution ($\approx 0.1 \text{ cm}^{-1}$) reflection-absorption spectrometer to measure the shape, cross section, and spectral position of the infrared absorption feature. iv) An optical detection scheme with increased dynamic range in order to measure changes on the order of 1 part in 10^5 in the two polarization components in an individual laser shot.

Each of the four technical issues mentioned above would have a substantial impact on the existing program, i.e. new adsorbates could be studied, faster processes could be followed, damage which accompanies laser-induced heating could be characterized, and smaller population changes could be seen. However, if all four objectives can be achieved, it will then be possible to measure vibrational relaxation rates at the surfaces of single-crystal metal surfaces. Our efforts to date in the four areas can be summarized as follows: i) We are currently exploring several methods for extending the tuning range available to the present laser system. We have generated $\approx 10\%$ of the required tunable infrared energy in the $5\mu\text{m}$ region by mixing the output of the existing optical parametric amplifier. A dye laser based on the Nd^{+3} YAG is being constructed to permit difference-frequency generation in LiIO_3 . ii) A shorter duration (≈ 2 ps FWHM) synchronously-pumped tunable dye laser is being amplified in order to generate sufficiently intense pulses for mixing in nonlinear crystals. iii) The feasibility of a high-resolution ($\approx 0.1 \text{ cm}^{-1}$ resolution) infrared reflection-absorption spectrometer based on a 20 ns Nd^{+3} YAG pumped difference-frequency generator is being explored. iv) In collaboration with Dr. A. Luntz of IBM, optical detection techniques with improved dynamic range (yet suitable for use in pulsed-laser experiments) are being explored.

H. Spin Polarization in Secondary-Electron Cascades in Ferromagnets (S. M. Girvin)

Recent experimental progress in the production and detection of spin-polarized, low-energy electrons is opening up new avenues of research in the study of both bulk and surface magnetism. One of the key requirements for a proper interpretation of many experimental measurements is an understanding of inelastic scattering and the production of secondary

electrons. In collaboration with Drs. D. R. Penn and S. P. Apell of the NBS Electron Physics Group, a theory has been developed of spin polarization in secondary-electron cascades in ferromagnets. We have found that measurement of the secondary polarization versus kinetic energy provides useful information about the inelastic scattering which cannot be obtained from traditional measurements of secondary intensity versus kinetic energy. In particular, we have found that the ratio of majority- to minority-spin inelastic lifetimes at an energy E is well approximated by the simple relation

$$\tau_{\uparrow}(E)/\tau_{\downarrow}(E) = \frac{1-p_B}{1+p_B} \frac{1+P(E)}{1-P(E)}$$

where P(E) is the measured secondary-electron polarization at energy E and p_B is the bulk polarization.

The lifetime ratios deduced from experimental measurements on Ni and Fe are shown in Figure 9. The rise in the ratio at low energies is due to the ability of minority electrons to scatter into the empty minority d-band states which arise from the bulk magnetization.

These results will prove useful in interpretation of photoemission and inverse-photoemission spectra and of polarized low-energy electron diffraction data. They also provide a testing ground for microscopic theories of inelastic and exchange scattering in ferromagnets.

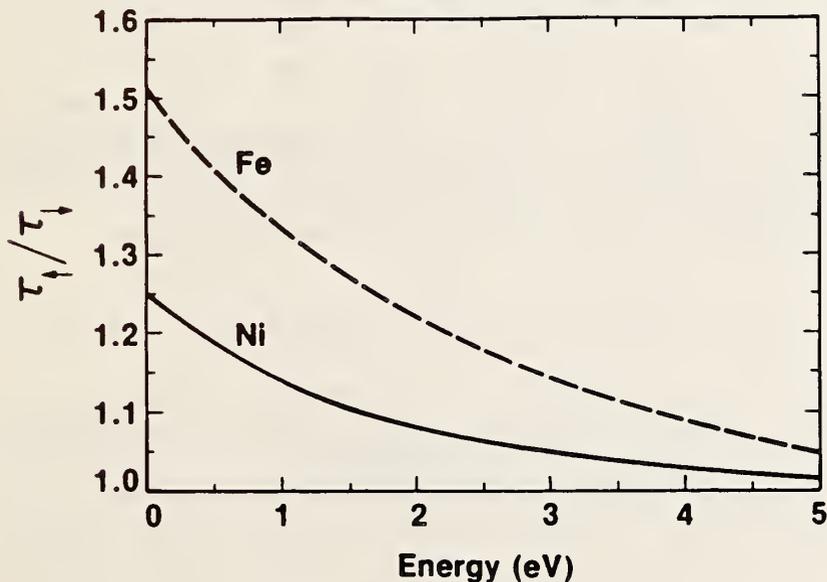


Fig. 9. Ratio of spin-up to spin-down lifetimes as a function of energy for Ni and Fe.

I. Theory of Dynamical Molecular Processes at Surfaces
(J. W. Gadzuk)

This project is part of a continuing effort directed to understanding both the static and dynamic behavior of atoms, molecules, solids, surfaces, radiation and their mutual interactions. This understanding comes from consideration of the microscope atomic-scale properties of individual entities as well as from larger-scale statistical properties of ensembles. Based upon our studies, phenomenological model theories are constructed which relate to the chemical physics and statistical mechanical behavior and to the intrinsic properties of relevant physico-chemical systems. In addition, a significant effort is invested in the study of the role of an actual measurement process in determining observed quantities in different surface spectroscopies. Ways in which measurement-process-specific quantities such as line shapes, satellite structures, etc. provide additional information on system dynamics are of considerable interest.

A large-scale theoretical effort has been underway aimed at the modeling of reaction dynamics at metallic surfaces and at interfaces of electro-chemical significance. Major focus in the past has been on the role of internal degrees of freedom (vibrational, rotational, and electronic) of molecules in determining energy flow and redistribution occurring in elementary molecular processes at surfaces.

Work has remained focused on the role of intra-molecular vibrational degrees of freedom in reactive surface dynamics. In these situations, energy must be directed in order to break bonds or be extracted to stabilize highly vibrationally excited species formed for instance at curve crossings where electronic rearrangement takes place. There has been significant progress in several different directions in the application of an analytic model (developed in collaboration with Dr. S. Holloway of Liverpool University) for obtaining classical trajectories of a diatomic molecular beam incident upon a surface and in which charge-transfer/curve-crossing events take place.

In collaboration with Dr. Holloway and Ms. M. Karikorpi of Liverpool University, calculations have been made of the multi-dimensional Landau-Zener probabilities for a two-state molecule/surface scattering event. We have obtained the correct branching ratios between scattered vibrationally-hot neutral molecules and negative-molecular ions. This is believed to be the first molecular-scattering calculation involving a physical surface which properly includes non-adiabatic coupling between electronic states of the molecule.

Computer codes have been constructed to calculate the classical trajectories of molecules over arbitrary potential-energy surfaces (PES) with emphasis again on those PES which include a curve crossing/seam. The example shown in Figure 10 represents a vibrationally cold I_2 molecule, with its molecular axis ρ in an orientation parallel to the physical surface, normally incident upon the surface with center-of-mass translational

energy $\approx 1\text{eV}$. Near the surface, I_2^- can form and this is characterized by an intra-molecular potential with large equilibrium separation and also by stronger bonding to the surface. The grill work structure at the top of Figure 10 is the PES. Contours of constant potential have been projected

IODINE

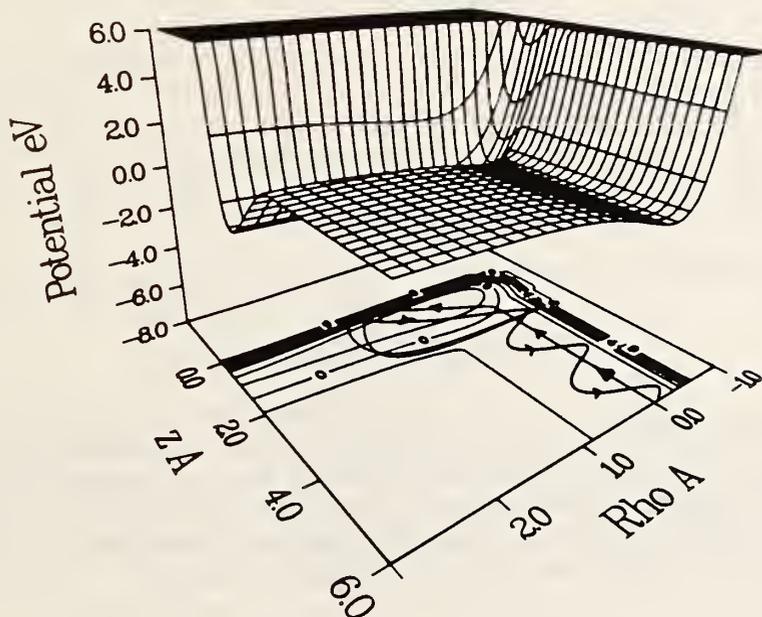


Fig. 10. A proposed potential energy surface (top) for an iodine molecule incident upon a physical surface in which dissociative adsorption is possible in the potential well at the surface for the molecule-surface separation $z \approx 1\text{\AA}$ along the intra-molecular coordinate ρ . Contour plot (bottom) of the PES in the (ρ, z) plane and a trajectory for a scattering event in which translational-to-vibrational energy redistribution occurs.

onto the (ρ, z) plane (bottom of Figure 10) where the trajectory is also shown. Note that the incident molecule becomes trapped for several oscillations as a negative-molecular ion before scattering, in this case with $\sim 0.7\text{ eV}$ translational energy. Amongst other things, we have calculated the probability for dissociative scattering as a function of incident kinetic energy, treating parametrically the well depth of the I_2^- /surface bond (the depth of the far left potential vs. z curve in Figure 10). Results are shown in Figure 11 together with experimental observations of Kolodney and Amirav. The significant point here is that, in both our theory and in the experiments, the dissociative scattering probability

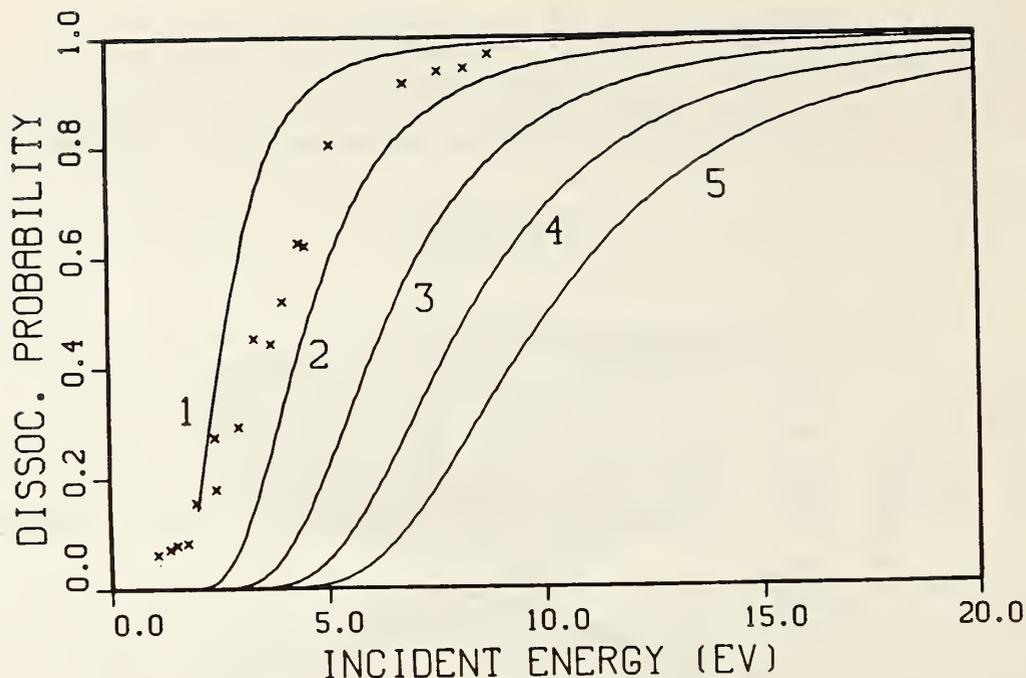


Fig. 11. Normalized probability for dissociative scattering of I_2 from a surface as a function of the kinetic energy of the incident I_2 molecular beam, treating the adsorption energy of I_2^- (in eV) parametrically. The points are reported results of Kolodney and Amiray for I_2 scattering from a MgO surface.

rises from zero at threshold to a saturation value over a kinetic energy range of - 4-6 eV. On the basis of the similarity between experiment and theory, it is believed that the charge-transfer mechanism is important in molecule-surface interactions.

We have developed further the "trajectorized wave-packet theory" reported last year to a point where it now satisfies microscopic reversibility and energy conservation (significant and ubiquitous flaws in most previous "imposed-trajectory" theories). At the request of the editor of "Comments on Atomic and Molecular Physics", a review article on "Surface Harpooning" was written. The principles of charge-transfer/curve-crossing collisions were sequentially developed for atom-atom, atom-molecule, atom-surface, and finally molecule-surface collisions. By working up in order of complexity, it was easy to see how one could use and adapt the results obtained in less complex collisional events.

Considerable progress has been made in the area of surface vibrational spectroscopy, at least in part because of the intimate connection between atom trajectories and vibrational spectra. A major

review article was written on "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces" in which the physics of the excitation process involved in the five most prevalent experimental techniques was developed from a single, unified point of view.

Further work on shape-resonances in electron scattering from molecules demonstrated how a shape-resonance/temporary-negative-molecular ion, created in an electron energy-loss experiment, not only leads to overtone enhancement in the intra-molecular excitations but also for any modes which have a component normal to the surface.

Finally, vibrational lineshapes and spectra of adsorbed molecules have been studied in terms of the quasi-periodic trajectories over multi-dimensional PES. This is a particularly prudent way to include the anharmonic effects which lead to dynamically interesting lineshapes because one can "see" what the oscillator is doing to acquire the line-shape. The lineshape or vibrational spectrum of an excited oscillator is

$$I(\omega) = \frac{1}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{2T} \left\langle \left| \int_0^{2T} Y(t) e^{i\omega t} dt \right|^2 \right\rangle$$

where $y(t)$ is the oscillator displacement as a function of time after initial excitation. As an example, the trajectory of an initially excited "harmonic" oscillator in the y direction ($Y_{in} = 0.1$, $X_{in} = 0.01$), which is anharmonically coupled to an x -oscillator with half the frequency is shown in the top of Figure 12. A number of well-defined y oscillations occur prior to a swing into the large-amplitude low-frequency oscillator and then return to y . This is a characteristic Fermi resonance and the vibrational spectrum shown in the bottom left of Figure 12 is a typical slightly-split doublet ($\Delta\omega/\omega \sim 0.1$ here). Increasing the initial displacement, hence anharmonicity, leads to a breakdown of quasiperiodicity. Thus chaotic motion prevails, as indicated in the spectrum shown in the bottom right of Figure 12 ($Y_{in} = 0.13$, $X_{in} = 0.01$). The main peak is very much reduced in height, broadened, and an erratic background appears. We are applying this methodology for determining vibrational spectra to current problems of active interest in the surface vibrational-spectroscopy community.

We plan to continue work in the area of surface reaction dynamics with near-term emphasis on the determination of self-consistent reaction trajectories, realistic electron-hole pair coupling constants, determination of energy-redistribution patterns amongst translational, vibrational, rotational, and electronic degrees of freedom of "reactant" molecules and electron and phonon modes of surfaces. Analyses are made for controllable dynamic and reactive conditions with synthesis of the various components of the elementary reaction theories into theories of experimentally realizable processes. Special emphasis will be placed on the phenomenon of dissociative surface processes and on the role of non-linear dynamics.

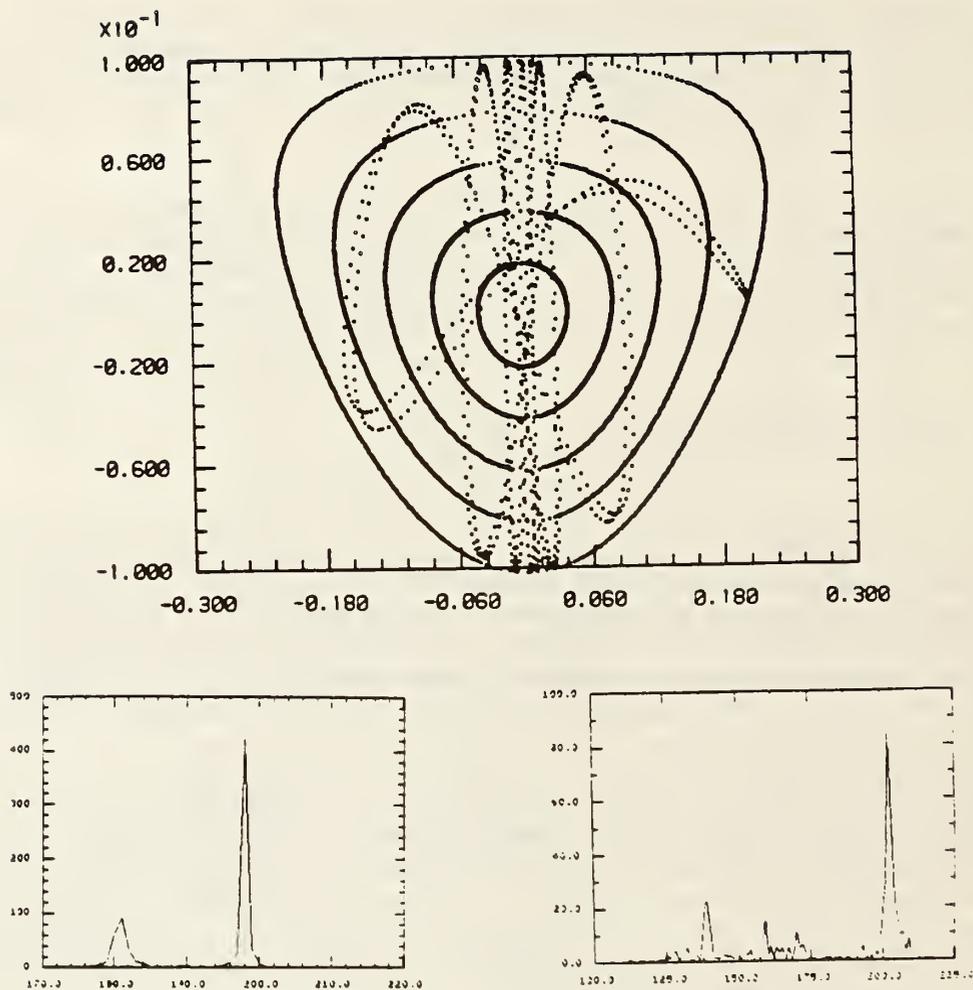


Fig. 12. Initial trajectory (top) for an excited oscillator oriented along the Y axis but anharmonically coupled to an X-oriented oscillator with half the frequency. Also shown are constant potential-energy contours. Vibrational spectra (bottom), $I(\omega)$ vs ω (arbitrary units), accompanying such an excitation for initial excitation below (left) and above (right) the chaotic threshold. Note the scale change between the two spectra.

In addition, analysis will be made, whenever possible, of novel experimental results. Current interest includes laser-assisted surface processes and state-to-state analysis, high-resolution surface vibrational spectroscopy, neutron spectroscopy of metal hydrides, and other experimental probes of non-adiabatic effects.

4. SURFACE COMPETENCE PROGRAM

W. F. Egelhoff, Jr., J. Fine, S. M. Girvin, T. J. Jach
R. Klein, T. E. Madey, A. J. Melmed, R. Stockbauer

The Surface Competence Program is a part of the NBS "Competence Program." The NBS program was introduced to provide long-term support of the establishment and maintenance of areas of excellence in science and technology contributing to the NBS mission and the projected needs of the NBS clientele.

The Surface Competence Program (NBS Task 26117) was established October, 1984 with two principal components, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". The initiation of this program represents a new focus on these topics. Each program component consists of several technical projects; some of these projects are extensions of activities in the Division that had existed prior to the start of this Competence Program while others have been launched this year. The principal objectives of each program component are described in the following two main Sections together with reports of the individual projects.

A. Novel Two-Dimensional Materials

In recent years an increasing awareness has developed of the important modifications in physical properties which occur in materials as they approach the ultra-thin two-dimensional limit. Some examples of unusual behavior discovered in such systems include the enhanced catalytic properties of a gold surface with two monolayers of platinum compared to bulk platinum, superconductivity of a silver monolayer on germanium, the quantum Hall effect, the enhanced magnetism in alternating monolayers of iron and cobalt, the electrical properties of metal-semiconductor junctions (Schottky barriers), and multiple quantum-well systems for optical logic devices. These examples suggest a whole new range of scientifically and technically important chemical and physical properties waiting to be explored in the two-dimensional regime. Concepts and methods developed in surface and interface science have been particularly valuable in many areas of application, and it is believed that these concepts and methods can be further developed and extended to two-dimensional systems with component thicknesses from one to one hundred atomic layers.

There exist major gaps in current understanding of the fundamental principles which govern the chemical and physical properties of layered structures in the two-dimensional limit. In this component of the program, it is planned to synthesize and determine the fundamental chemical and physical properties of ultrathin layered materials with layers so thin (a few atoms thickness) that they exhibit two-dimensional behavior. Knowledge of the factors influencing the growth and properties

of ultrathin layered systems is expected to allow optimization of desired chemical and physical characteristics and will thus benefit a number of scientific fields ranging from catalysis to novel semiconductor devices.

We are performing work in four project areas. First, we are planning to develop the techniques needed to synthesize, by alternating monolayer deposition, a new class of materials: non-equilibrium ordered alloys. The structural properties of these materials as grown and during thermal processing will be investigated by x-ray and electron diffraction. The chemical reactivity, catalytic activities, and magnetic properties of these materials will also be investigated. Second, we plan to determine the microstructure and microcomposition of candidate layered structures by atom-probe and field-ion microscopy methods with emphasis on the interface region. These techniques provide composition and structure data with near-atomic spatial resolution. Third, we will apply modern many-body theoretical techniques to the study of the quantum Hall effect, magnetism, and other electronic properties of layered structures. Finally, we are planning to develop techniques for the study of the growth and morphology of modulated structures using glancing-incidence diffraction of x-rays from a synchrotron source and other extensions of modern surface methods.

1. Surface and Interface Chemical Physics of Ultrathin Films
(W. F. Egelhoff, Jr.)

Interest in ultrathin metal films (down to the two-dimensional limit of one atomic layer) on the part of the surface-science community has greatly increased in the past several years as it has become clear that an understanding of such structures will contribute to solving a wide range of problems in surface science. Among these are an understanding of the differences between surface and bulk electronic structure, the changes of surface electronic structure associated with chemisorption, the basis of surface magnetism, the modification of surface-layer properties by the substrate, the relationship between electronic structure and epitaxial growth, and the surface properties of alloys. The experimental program presently underway is using an integrated approach to study single-crystal surfaces, alloys and ultrathin films to contribute to an understanding of all of the above problems.

We reported last year on the discovery of a new aspect of x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) and have termed it the "searchlight effect". The searchlight effect is manifested in single-crystal samples by enhanced XPS and AES peak intensities along nearest-neighbor and next-nearest-neighbor directions in the lattice.

The searchlight effect is a powerful, new probe of short-range order and is ideally suited for studying a variety of problems associated with ultrathin films, surfaces, and interfaces. We now have the opportunity to perform real-time studies of surface morphological and compositional dynamics such as clustering of overlayers, surface segregation, and surface alloying or interdiffusion at interfaces. Although these

phenomena are interesting in their own right, we are planning to investigate them in association with our current primary objective of synthesizing a new class of materials, non-equilibrium ordered alloys, by epitaxial growth of alternating metal monolayers. This work has the potential for opening up a whole new area of materials science. The XPS searchlight effect is a near-perfect tool for diagnosing, in real time, any growth processes that interfere with the desired synthesis and should thus aid greatly in recognizing and overcoming barriers. We anticipate the capability of producing novel material properties by tailor-making the lattice structure. Later, we expect to characterize the materials with x-ray diffraction and electron microscopy and to study their chemical reactivity, catalytic activity, and magnetic properties.

We are in the process of improving our XPS instrument to carry out the work just described. Changes in electron optics and detection will provide substantially better operating characteristics. These changes will, in part, permit application of the XPS searchlight effect to higher electron energies than the conventional XPS range where it should have increased diagnostic power. We are also designing a system of ultrahigh-vacuum ovens to provide the sources with constant metal vapor flux that are needed to grow high-quality films with alternating monolayers by molecular-beam epitaxy.

The source of the angular anisotropies of electron emission in XPS and AES that give rise to the searchlight effect have been investigated using single-scattering calculations. These calculations, performed for copper films as a function of thickness, demonstrate that the enhancements are associated with forward scattering by nearest-neighbor and next-nearest-neighbor atoms in the lattice. The searchlight effect can thus be used with confidence as a structural probe. The effect, however, is a serious complication in the conventional method of measuring (and using) electron attenuation lengths with single-crystal specimens. Further details of this analysis are given in Section 2.A.4.

Work has continued on the development of the equivalent-core approximation (ECA) as an interpretative tool for analyzing core-level binding-energy shifts. Figure 13(a) shows how the Ni $2p_{3/2}$ core-level shift induced by the adsorption of CO is governed by total-energy considerations that can readily be understood with the ECA. In the final state, a fully-screened core hole on Ni becomes (by the ECA) the chemical equivalent of Cu. We consider the difference between final states with clean or CO-covered Cu, as in Figure 13(a). Since there is a choice in the final state between CO on a Ni atom and CO on the Cu atom, we can immediately use the greater Ni-CO bond strength to predict that the final state leaving Cu clean will have the lower total energy. The Ni $2p_{3/2}$ core-level binding energy is just the energy to get from the initial state to the indicated final states. We therefore deduce that the clean Ni must exhibit the smaller binding energy and the CO-induced shift must be to larger binding energy. Figure 13(b) shows the use of the ECA in

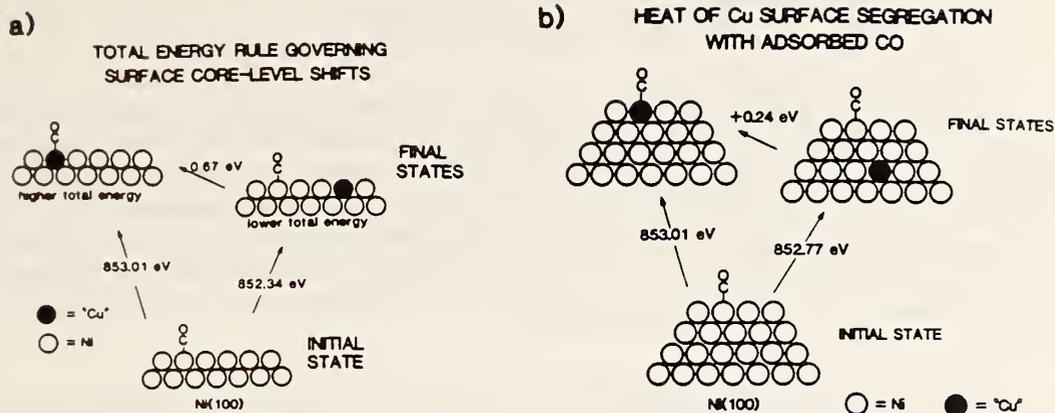


Fig. 13. (a) Illustration of how total energy considerations govern the CO-induced surface core-level shift in Ni(100). (b) Illustration of how the bulk-to-surface core-level shift can predict the heat of Cu surface segregation to a surface site with adsorbed CO.

determining from the bulk-to-surface Ni $2p_{3/2}$ core-level shift that Cu segregation to a CO-covered surface site is an endothermic process by 0.24 eV (5.5 kcal/mole). This result is in sharp contrast to the case of Cu segregation to a clean Ni surface which is 0.43 eV (10 kcal/mole) exothermic. The adsorption of CO will therefore drive Cu into bulk Ni.

Finally, a major invited article titled "Core-Level Binding-Energy Shifts at Surfaces and in Solids" has been completed for Surface Science Reports. This review article will, as it appears, be approximately 200 pages long and contain over a thousand references. The article consists of a review of the theoretical principles of core-level shifts and a selection of the most illustrative, experimental case studies. The theoretical principles section is written with the experimentalist in mind and explains the essential concepts such as core eigenvalues, initial-state contributions, total energy differences, charge-transfer screening, and polarization and dielectric screening without resorting to the usual, opaque mathematics. Particular attention is paid to the principles of the reference-level problem since many important fine points have often been glossed over in previous descriptions. The section on experimental case studies contains selected results which illustrate, in the most clear-cut manner possible, the basic mechanisms governing core-level shifts. The topics include atomic coordination number, charge transfer, Madelung potentials, cluster size, surface work function, image-charge and charge-transfer screening, band bending, and sample charging. In this section, particular attention is paid to the relative merits of the two basic conceptual frameworks for interpreting core-level shifts, the equivalent-core-energy-cycle framework and the initial-state--final-state framework.

2. Microcomposition and Microstructure of Thin Films (A. J. Melmed and R. Klein)

This effort is directed to the measurement of microcomposition in relation to microstructure of thin layers on well-characterized solid substrates and the determination of interfacial diffusion. The methods of investigation for these purposes are field-ion microscopy (FIM), capable of qualitative atomic structural determination, and atom-probe analysis for compositional depth-probing on an atomic scale. Both in situ and ex situ specimen preparation will be used in order to vary widely the layer-formation process parameters.

During this reporting period, the unique capability of FIM to characterize the microstructure of novel materials was demonstrated. One of the recently discovered class of rapidly solidified aluminum-based alloys, which appeared by electron diffraction in the transmission electron microscope (TEM) to have icosahedral long-range order and no translational symmetry, was made available to us. A considerable amount of theoretical work has been done to explain and predict the relevant atomic structure. Thus far, several theoretical models have predicted correctly most of the observed diffraction features, but no complete description of atomic positions has been given. The alloy, approximately Al_6Mn , was provided to us in the form of pieces of very brittle ribbon, a few millimeters on a side and some 0.040-0.050 mm thick, and presented some complications in specimen preparation. However, we succeeded in obtaining reproducible FIM images which clearly showed that the material has a phase in real space with structure consistent with icosohedral long-range order; that is, appropriate two-, three- and five-fold symmetries are present, over a lateral distance of about 200 nm, and no translational symmetry is evident. Also, we found no evidence for multiple twinning, the major counter-viewpoint to the acceptance of real icosohedral symmetry. In those regards, the FIM results clearly agree with the TEM results. Additionally, the FIM images showed that the microstructure is replete with micro-defects. Atomic disSection of the material by field evaporation clearly showed that these features prevailed through a depth of at least 300 nm. Further microscopy remains to be done in an effort to determine the details of atomic packing in this complex material.

The construction of our energy-corrected atom-probe (ECAP), which will be used for determining composition profiles through thin layers and layer/substrate interfaces, has been recently completed. All features of the ECAP have been tested and found to function qualitatively as expected. Initial quantitative evaluation has indicated that the mass resolution is better than anticipated in the lower-resolution Section of the ECAP; that is, $M/\Delta M$ appears to be at least ~ 250 and possibly is as high as 500 (compared to an expected value of about 150). Quantitative evaluation of the high-resolution Section has been thwarted so far by a mechanical misalignment introduced during the ECAP fabrication.

We have found it increasingly useful to combine our atom-probe analyses with the imaging capability of TEM (in collaboration with colleagues in the NBS Metallurgy Division). The atom-probe-FIM--TEM combination is extremely powerful in providing microscopy with a wider range of contrast and magnification than available to the separate techniques. For this purpose, we have developed a specimen holder which allows us to shuttle specimens between the atom-probe FIM and the TEM. Using this extended capability, we have begun microcomposition and microstructure analyses of nickel-based superalloys (of interest as turbine-blade materials) and of a newly developed class of Al-Li-Cu alloys.

During the next year, it is planned to complete the quantitative evaluation of the ECAP and to bring the associated electronics to a convenient working arrangement. Presently, the ECAP is operated using the timing electronics of the general-purpose atom-probe FIM developed earlier which is awkward for the user. A more appropriate system is partially developed.

Further microscopy and possibly atom-probe analysis of the icosahedral-symmetry alloys and related materials are planned. Atom-probe analyses of nickel-based and aluminum-based alloys will also be done. It is hoped that an ultra-high-vacuum FIM can be assembled specifically for in situ thin-layer deposition and microstructure characterization.

After full evaluation of the ECAP performance, a program of depth-probe analyses of thin-layer/substrate combinations will be undertaken. Metal/metal systems prepared by alternate-layer vapor deposition will be investigated in order to characterize the interfacial composition and to determine the extent of intermixing. Appropriate choices of elemental metals and preparation parameters will be made in concert with other related experiments (e.g., Section 4.A.1 above).

3. Theory of the Quantum Hall Effect (S. M. Girvin)

Artificial semiconductor superlattices (heterostructures or multi-quantum wells) consisting of alternating atomically smooth layers of GaAs and GaAlAs are among the most novel and successful two-dimensional materials. By suitable doping one can create at the GaAs-GaAlAs interface a two-dimensional electron gas which exhibits many interesting effects.

One of the most remarkable phenomena which has been observed in the GaAs-GaAlAs system is the quantum Hall effect. At very high magnetic fields (~10 T) and low temperature (< 4 K), the Hall resistance of the two-dimensional electron gas takes on universal quantized values of the form h/e^2i where h is Planck's constant and e is the elementary charge. The quantum number i is an integer or simple rational fraction. Associated with this quantization is the existence of persistent nearly

dissipationless currents similar to those occurring in superconductors and superfluids. These unexpected findings have stimulated considerable experimental and theoretical work at many laboratories.

In collaboration with Drs. A. H. MacDonald (National Research Council, Ottawa) and P. M. Platzman (AT&T, Bell Laboratories, Murray Hill) a "magneto-roton" theory has been developed of the collective excitations in these fractional quantum-number states. This theory is closely analogous to the Feynman theory of superfluid helium and provides new insight into the physics underlying the persistence of currents.

The collective modes at long wavelength are predicted to be phonons (density waves) and magneto-rotons analogous to the roton excitations in superfluid helium. The predicted mode spectrum is shown in Figure 14. Independent numerical calculations on model systems by Dr. F. D. M. Haldane of AT&T Bell Laboratories have shown that this magneto-roton theory is remarkably accurate. Figure 14 illustrates the good agreement between the predicted mode energy and Haldane's numerical results. One of the advantages of our theory is its analytic simplicity which allows one for the first time to compute quite easily experimentally relevant and

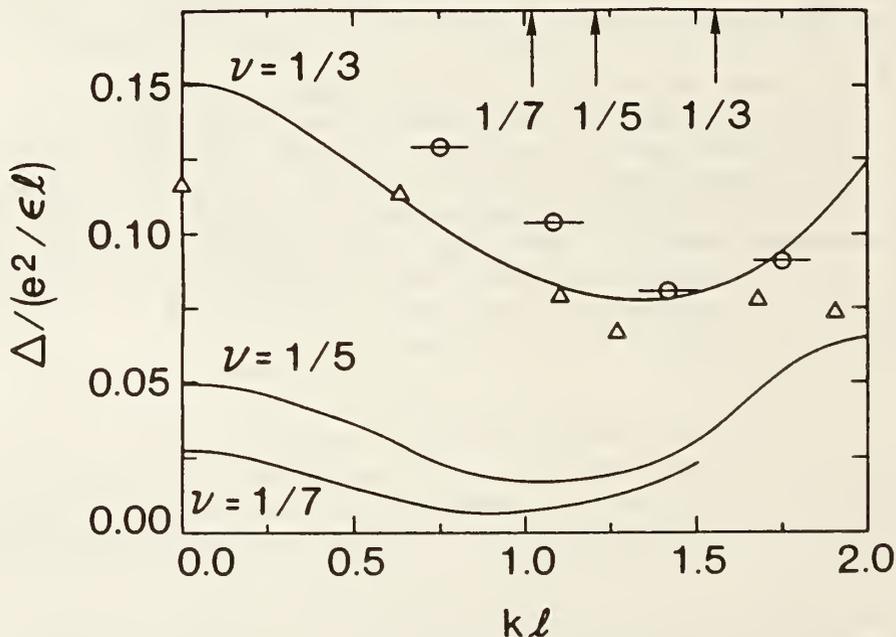


Fig. 14. Collective excitation energy Δ versus wave vector for $\nu = 1/3$, $1/5$, and $1/7$. The solid lines are analytic results of the magneto-roton theory. The circles and triangles are from numerical calculations for $\nu = 1/3$ on small spherical and hexagonal systems by Haldane and Rezayi. Arrows indicate position of reciprocal lattice vectors of the Wigner crystal at the appropriate densities.

previously inaccessible quantities such as the dielectric response. Experimental attempts to observe the predicted magneto-roton excitations via the dielectric response are currently under way in two separate groups at AT&T Bell Laboratories.

This magneto-roton theory nicely complements earlier work we have done on the Wigner crystallization transition. As the magnetic field is increased, the magneto-roton mode goes "soft" at the wave vector corresponding to the Wigner-crystal reciprocal-lattice vector. The critical field at which the magneto-roton softening makes the liquid state unstable agrees quite well with our previous predictions for the field at which the Wigner crystal becomes stable. Hence the combination of these two theories gives us a much deeper and more complete understanding of the liquid-solid transition in this system.

Future work in this area will address questions of the finite-temperature statistical mechanics of the quantum Hall effect and the effects of disorder. Another project which will take place in the coming year is the organization of a quantum Hall effect lecture series at the University of Maryland. In collaboration with Professor R. E. Prange, plans are being made to edit and publish the lecture notes of the invited speakers as a Springer-Verlag book. This book is intended to be a tutorial introduction to this rapidly expanding field for both experimentalists and theorists.

Another area of planned future work concerns the field of metallic superlattices. Dr. Michael DeWeert will be joining the Division as an NRC postdoctoral fellow. His area of expertise is superconductivity, proximity effects, and related phenomena in metallic superlattices. Close interaction is expected with the superlattice experiments in the Division and with the proximity effect work in the NBS Temperature and Pressure Division.

4. Dynamical Diffraction of X-Rays from Crystal Surfaces at Glancing Incidence
(T. J. Jach)

The structure and registry of adsorbed atoms with respect to the underlying crystal lattice remains one of the major concerns of surface science. Diffraction techniques such as low-energy electron diffraction provide some of this information, but some foreknowledge of potential sites of the atom and extensive calculation are usually required. We have developed a new technique using the dynamical diffraction of x-rays in a glancing-incidence geometry to provide the same type of information. The technique is surface sensitive but could be employed at interfaces as well.

Although the theory for dynamical x-ray diffraction has been developed previously, it had not been tested experimentally since the necessary experiments require an intense source of monochromatized x-rays (e.g., from a synchrotron source), a well-collimated beam, and a specimen

crystal with a smooth, defect-free surface. In collaboration with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group and Drs. M. Bedzyk and G. Materlik of the Deutsches Elektronen Synchrotron (DESY) at Hamburg, an experiment was conducted last fall at DESY to test the theory. We observed surface diffraction from Ge(220) planes normal to the (111) surface at 8 keV with angles of incidence as low as 1 milliradian. X-ray beam collimation at the Bragg angle was about 5 microradians (Figure 15). This extreme collimation, possible only on a synchrotron light source, allowed us to obtain data which turned out to fit the theory very well.

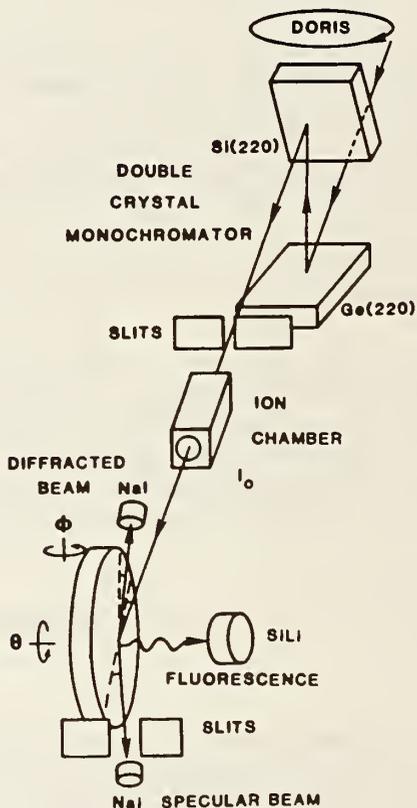


Fig. 15. Experimental set-up for grazing-incidence x-ray diffraction.

During the past year we have done considerable data analysis which gave us a great deal of insight into surface dynamical diffraction theory. Because we are able to diffract an x-ray beam from a crystal at incidence angles less than the critical angle for total reflection (~ 4 milliradians), the x-rays inside the crystal are only evanescent (exponentially-decaying) waves. There are two waves, however, and their linear combination at the crystal surface forms an x-ray standing wave.

Slight changes in the angle of incidence or deviations from the Bragg angle translate this standing wave back and forth on the surface, selectively exciting surface atoms whose fluorescence was observed. The interference process which makes this possible is illustrated in Fig. 16(a) where the specularly reflected beam is shown to have either a strong absorption or a maximum at the Bragg condition depending on the angle of incidence.

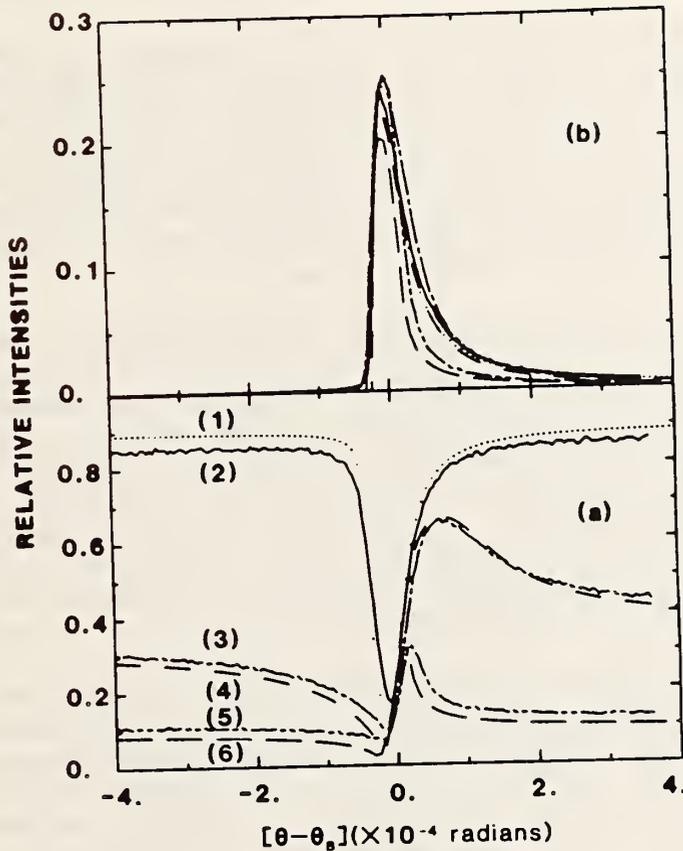


Fig. 16 Intensities of (a) specular beam and (b) diffracted beam as a function of deviation from the ideal Bragg angle θ_B for various fixed angles of incidence ϕ . Curves 2, 3, and 5 are experimental results and curves 1, 4, and 6 are results from dynamical diffraction theory. The measurements and calculations are for three angles of incidence: $\phi = 4.74$ milliradians, less than the critical angle for total reflection (curves 1 and 2); $\phi = 5.55$ milliradians, at the critical angle (curves 3 and 4); and $\phi = 6.35$ milliradians, greater than the critical angle (curves 5 and 6).

These initial experiments were carried out in helium at atmospheric pressure and we are building a chamber to continue the work in ultra-high vacuum. We intend to measure position-dependent fluorescence, photoemission, and Auger-electron decay from surface atoms. To this end, we have already built a new bent-crystal ultrahigh vacuum (uhv) x-ray spectrometer. The principal task during the coming year will be to design and build a uhv crystal goniometer which will be accurate to a few seconds of arc. The equipment is designed to be used on our new focussed x-ray beam line, X-24A, at the Brookhaven National Synchrotron Light Source.

B. State Characterization of Energetic Species Ejected from Surfaces

Specific state characterization of desorbed and ejected species from surfaces, whether induced by sputtering or by electron and photon bombardment, is still rare. It is now possible to address such dynamical surface interactions using laser techniques to determine the energy state, velocity, and angular distributions of all the ejected species--especially the neutrals which are the most abundant. Such studies can provide detailed microscopic information concerning energy transfer in these excitation/interaction processes.

The objective in this component of the program is to understand the excitation dynamics by which atoms and molecules are desorbed from surfaces in ion-sputtering processes as well as in electron- and photon-stimulated processes. Detailed characterization of the internal energy, kinetic energy, and desorption thresholds of desorbed species will provide a microscopic understanding of the nature of the electronic excitations leading to desorption due to collisions with electrons, photons, and ions. Angular distributions will provide direct structural information concerning the surface geometry, as well as information concerning energy transfer during the collisional interaction.

We are combining ultrahigh-vacuum surface-science techniques with state-of-the-art laser spectroscopy in several experiments involving electron-stimulated desorption (ESD), photon-stimulated desorption (PSD), and ion sputtering. Specifically, we propose to use multiphoton ionization and other laser-spectroscopic techniques to detect and analyze neutral species released from crystalline surfaces by electron, photon, and ion bombardment. These measurements will provide unique insights into the mechanisms of desorption induced by both electronic transitions and by direct momentum transfer. Measurements of neutral angular distributions will be compared directly with ion angular distributions using a new two-dimensional display analyzer, thus providing a detailed description of competing desorption pathways.

We are performing work in three project areas. First, we are designing an experiment in which laser-spectroscopic techniques will be used to determine the energy states of neutral atoms and molecules sputtered from surfaces by ion bombardment. Second, we are collaborating with scientists at Vanderbilt University on a similar experiment in which

neutral species desorbed from surfaces by electron or photon excitation will be detected and characterized. This experiment may lead later to similar work at NBS. Finally, we are constructing a new type of display analyzer to measure angular and energy distributions of neutral species desorbed from surfaces by electrons or photons to obtain surface-geometry information and to test theories of ejection mechanisms. Close contact is made with the related experimental and theoretical projects in the Division described in Sections 3.B, 3.D, 3.G and 3.I.

1. Energy States of Neutral Species Sputtered from Surfaces (J. Fine)

Energetic ion-surface collisions generate extensive near-surface collision cascades in a solid. The energy transfer and atomic excitations that take place as a result of such collisions are not well understood in part because, until rather recently, the primary method for monitoring these collision phenomena was to measure macroscopic effects such as the total sputtering yield. The collision cascade causes the ejection of atoms, ions, electrons, and photons from the surface but it has only been in the past few years that measurements of the ejected particles or radiation have been utilized to obtain detailed information of specific atomic collisions that take place in condensed materials.

In recent experiments in which aluminum or silicon targets were bombarded by argon ions, we have shown that the Auger decay of collisionally excited Al or Si atoms can take place outside the solid depending on the distance from the surface (within the material) at which the excitation occurred, the atom's velocity, and the lifetime of the atomic excitation. As a result of our Monte-Carlo calculation to analyze these experiments, we expect that such sputtered atoms will have rather high kinetic energies - extending up to hundreds of electron volts. Collisions capable of transferring this much energy and creating inner-shell (2p) excitation can generate sputtered atoms (ions) which are in highly excited states. Such energy-transfer and excitation mechanisms are basic to our enhanced understanding of collisional processes in condensed materials. Information is required of those atomic processes which lead to electron promotion, excitation and ionization, and particle ejection. It is now possible to obtain this type of information by: (1) probing specific ejected (sputtered) atoms via resonant, multiphoton laser techniques; (2) monitoring the Auger-electron de-excitation of ejected atoms as well as those which decay inside the solid; (3) analyzing the emitted secondary-electron energy distributions. Progress made during the first year of this project in each of these areas is described below.

(a) Laser Spectroscopy of Sputtered Atoms and Ions

In collaboration with Drs. L. J. Moore (NBS Inorganic Analytical Research Division) and T. B. Lucatoro (NBS Radiation Physics Division), a new series of experiments has been planned and designed to determine the kinetic energy distributions of specific sputtered atoms (ions) and their states of excitation. Resonance multiphoton

laser-ionization schemes have been developed to detect sputtered atoms in specific excited states and time-of-flight techniques will be used to measure their kinetic energy distributions. Pulse timing and gating sequences have been designed and estimates made of signal intensity indicate that such measurements are feasible. A new apparatus has been designed for this experiment and consists of an ultrahigh vacuum chamber (that allows ion-beam-angle-dependent measurements to be made) connected to a time-of-flight analyzer. This chamber, which is under construction, will be coupled to two ultraviolet pulsed-laser systems. We plan to investigate atoms (ions) sputtered from surfaces of magnesium, aluminum, and silicon and to determine their charge state, excitation state, and kinetic energy distributions.

(b) Auger-Electron De-Excitation of Sputtered Atoms

In collaboration with Drs. C. Le Gressus and J. P. Durand (Centre d'etudes Nucleaires de Saclay, France), a new series of measurements were begun to investigate the Auger-electron emission from ion-bombarded single-crystal aluminum surfaces. Aluminum (100) and (111) surfaces were bombarded with argon ions and the dependence of atomic-like and band-like Auger-electron emission was monitored as the crystals were rotated about an axis normal to the surface. Preliminary results indicate a very marked change in Auger-electron emission intensity as a function of rotation angle. Intensity minima correspond to geometrical conditions where the incident ion beam is aligned with a string of atoms (i.e., there is a shadowing of underlying atoms by the outermost surface atom of a given string). Measurements of this phenomena are still in progress in Saclay; we anticipate extending this investigation of collisional excitation processes in single-crystal solids at NBS.

(c) Secondary-Electron Energy Distributions Due to Ion Bombardment

In collaboration with Dr. I. Terzic (Boris Kidric Institute, Belgrade, Yugoslavia), an experiment has been designed to study the secondary-electron energy distributions that result from Ga^+ -Ga collision at ion energies from 20 to 60 keV. Previous measurements at NBS indicate that collisional excitation may account for the high energy (> 100 eV) emitted electrons observed. An apparatus is presently under construction in Belgrade which will enable us to examine inner-shell excitation thresholds in this system.

2. Electron- and Photon-Stimulated Desorption of Neutral Species Using Laser Detection Techniques
(T. E. Madey)

In a collaborative effort with Prof. N. Tolk at Vanderbilt University, we have initiated measurements to characterize the mechanisms by which neutral species are excited and desorbed from surfaces using electron- and photon-stimulated desorption (ESD/PSD).

The majority of species removed from surfaces via ESD and PSD are neutral atoms and molecules. However, virtually all measurements of the energy and angular distributions of desorbing species have been of the more-easily-detected minority ionic species; only recently have laser techniques been applied to the detection of neutral species. The few measurements made to date have concentrated on desorption from poorly characterized surfaces, or radiation-induced decomposition of bulk solids (e.g., alkali halides).

Our experiments are designed to search for and characterize the ESD of both ground-state and excited Li and Na atoms desorbed from fractional-monolayer films of Li and Na adsorbed on both clean and oxygen-covered W(100) surfaces. We will employ laser-induced fluorescence to detect the ground-state neutrals, and light emission following metastable deexcitation to detect excited neutral species. A later stage of the measurements will involve the use of synchrotron radiation to determine the threshold energies for desorption via photon-stimulated desorption. The choice of experimental systems for these first studies (Na, Li on O/W(100)) is based on previous related experiments and the theoretical interest in these conditions.

2. Angular and Energy Distributions of Desorbed Ionic Species (R. Stockbauer and T. E. Madey)

We have designed a special analyzer to measure simultaneously the angular, energy, and mass distributions of ions desorbed from surfaces. The analyzer will in addition be used for angle-resolved photoemission.

The construction of a new angle-resolving, display-type ion and electron energy analyzer is nearing completion. This instrument is based on the IBM design of Dr. D. Eastman. After completion of the analyzer and assembly, the analyzer will undergo initial testing in the laboratory using an electron impact source. The video processing software which will display the two-dimensional data in an appropriate form will be developed during this initial testing. This same software will be used to process similar two-dimensional data from a video system to be installed for our ESDIAD project (Section 3.B).

The initial test experiments using the new analyzer will be a series of quantitative ESDIAD (Electron Stimulated Desorption-Ion Angular Distributions) studies of small molecules adsorbed on metal surfaces. The test systems will include NH_3 and H_2O on Ni(111), as well as the coadsorption of each of these molecules with electronegative (O, S, Br) and electropositive (K, Na) additives. Some of these systems have been studied previously but a number of longstanding and important fundamental questions remain for which the new analyzer can provide quantitative answers. Experiments are planned to address the following questions.

- o What are the angular profiles of the ion beams?
- o Is there quantitative structural information in individual ESDIAD beam shapes?
- o How do the angular profiles of individual ion beams vary with adsorption coverage and the presence of co-adsorbates?
- o How do the ESDIAD patterns vary as a function of electron excitation energy?
- o Are the ion energy distributions a function of desorption angle?
- o How do measured ion trajectories compare with theory?

In later experiments at the NBS synchrotron radiation source SURF-II, the analyzer will be used in angle-resolved photon-stimulated desorption studies of clean and adsorbate-covered oxide surfaces. Desorption thresholds and energy dependences will be correlated with angle-resolved electron spectroscopic measurements (ultraviolet photoelectron spectroscopy, constant-initial-state, constant-final-state measurements). These measurements will be the first detailed, angle-resolved mechanistic studies of photon-induced bond-breaking processes at surfaces.

5. PUBLICATIONS

(a) Publications of Past Year

- Armstrong, R. A. and Egelhoff, Jr., W. F., "An Analysis of Angular Dependent XPS Peak Intensities," *Surf. Sci.* 154, L225 (1985).
- Bange, K., Madey, T. E. and Sass, J. K., "The Adsorption of Oxygen on Ag(110): A New View of Structure and Bonding," *Chem. Phys. Lett.* 113, 56 (1985).
- Bange, K., Madey, T. E. and Sass, J. K., "Characterization of OH(ad) Formation by Reaction Between H₂O and O(ad) on Ag(110)," *Surf. Sci.* 152/153, 550 (1985).
- Bertel, E., Ramaker, D. E., Kurtz, R. L., Stockbauer, R. and Madey, T. E., "Photon Stimulated Desorption of H⁺ Ions From OH on Ti and Cr: Comparison with Bulk Solid H₂O," *Phys. Rev. B Rapid Commun.* 31, 6840 (1985).
- Bertel, E., Stockbauer, R., Kurtz, R. L., Madey, T. E. and Ramaker, D. E., "The Decay Channels of the 3p Resonance in the 3d Transition Metals and Their Relevance to the Mechanisms of Electron and Photon Stimulated Ion Desorption," *Surf. Sci.* 152, 776 (1985).
- Bertel, E., Stockbauer, R., Kurtz, R. L., Madey, T. E. and Ramaker, D. E., "3p-Core Hole State Sensitivity in Ion Desorption from Oxidized Cr," in Desorption Induced by Electronic Transitions, II, eds. W. Brenig and D. Menzel, *Springer Series in Surface Sciences, Vol. 4* (Springer-Verlag, Heidelberg), 84 (1985).
- Bertel, E., Stockbauer, R., Kurtz, R. L., Ramaker, D. E. and Madey, T. E., "Resonant Photoemission and the Mechanism of Photon Stimulated Ion Desorption in a Transition Metal Oxide," *Phys. Rev. B* 31, 5580 (1985).
- Bozso, F., Yates, Jr., J. T., Arias, J., Metiu, H. and Martin, R. M., "A Surface Penning Ionization Study of the CO/Ni(111) System," *J. Chem. Phys.* 78, 4256 (1983).
- Butler, J. J., Holland, D. M. P., Parr, A. C. and Stockbauer, R., "A Threshold Photoelectron-Photoion Coincidence Spectrometric Study of Dimethylether (CH₃OCH₃)," *Int. J. Mass. Spectro. Ion. Phys.* 58, 1 (1984).
- Casassa, M. P., Heilweil, E. J., Stephenson, J. C. and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation of Molecules on Surfaces: Hydroxyl Groups on Silica Surfaces," *J. Vac. Sci. Tech.* A3, 1655 (1985).
- Cavanagh, R. R. and King, D. S., "Laser Studies of Surface Chemical Reactions," in Chemistry and Physics of Solid Surfaces V, Springer Series in Chemical Physics 35 (Springer-Verlag, New York), 141 (1984).

- Ceyer, S., Melmed, A. J., Carroll, J. J. and Graham, W. R., "On the Atomic Structure and Optical Constants of (001) Tantalum," Surf. Sci. 144, L444 (1984).
- Ceyer, S. and Yates, Jr., J. T., "Ammonia Adsorption on the Ag(311) Surface," Surf. Sci. 155, 584 (1985).
- Ceyer, S. and Yates, Jr., J. T., "Orientation of CH₃NC Adsorbed on Ag(311)," J. Phys. Chem. 89, 3842 (1985).
- Ciszewski, A. and Melmed, A. J., "Epitaxial Growth and Some Properties of Samarium Crystals on Tungsten," J. de Physique 45, C9 (1984).
- Ciszewski, A. and Melmed, A. J., "Epitaxial Crystal Growth of Gadolinium on Tungsten," Surf. Sci. 145, L471 (1984).
- Ciszewski, A. and Melmed, A. J., "Surface Self-Diffusion of Dysprosium and Gadolinium," Surf. Sci. 145, L509 (1984).
- Ciszewski, A. and Melmed, A. J., "Epitaxial Crystal Growth of HCP Metals on BCC Metals: Dysprosium on Tungsten," J. Crystal Growth 69, 253 (1984).
- Cox, D. F., Semancik, S. and Szuromi, P. D., "The Interaction of Water Vapor with Tin Oxide," Proceedings of the International Conference on Solid-State Sensors and Actuators-Transducers, Boston, MA, 385, (1985).
- Doering, D. L. and Semancik, S., "Orientational Ordering in a Strongly Chemisorbed System: Na on Ru(001)," Phys. Rev. Lett. 53, 66 (1984).
- Egelhoff, Jr., W. F., "A Core-Level Binding-Energy Shift Analysis of CO, H, and O Adsorption on Cu-Ni Surfaces," J. Vac. Sci. Tech. A3, 1305 (1985).
- Egelhoff, Jr., W. F., "A New Tool for Studying Epitaxy and Interfaces: The XPS Searchlight Effect," J. Vac. Sci. Tech. A3, 1511 (1985).
- Egelhoff, Jr., W. F., "Angle Resolved XPS of the Epitaxial Growth of Cu on Ni(110)," in The Structure of Surfaces, M. A. Van Hove and S. T. Tong, eds., (Springer, Berlin), 199 (1985).
- Egelhoff, Jr., W. F., "The XPS Searchlight Effect: A New Analytical Tool for Layered Structures, Epitaxy, and Interfaces," in Layered Structures, Epitaxy and Interfaces, MRS Proceedings, Vol. 37, J. M. Gibson, ed. (Materials Research Society, PA), 443 (1985).
- Fine, J., Lindfors, P. A. Gorman, M. E., Gerlach, R. L., Navinsek, B., Mitchell, D. F. and Chambers, G. P., "Interface Depth Resolution of Auger Sputter Profiled Ni/Cr Interfaces: Dependence on Ion Bombardment Parameters," J. Vac. Sci. Tech. A3, 1413 (1985).
- Fine, J. and Navinsek, B., "Characterization of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," J. Vac. Sci. Tech. A3, 1408 (1985).

- Gadzuk, J. W., "Surface Harpooning," Comments on Atomic and Molecular Physics, 16, 219 (1985).
- Gadzuk, J. W., "Resonance Vibrational Excitation in Electron-Energy Loss Spectroscopy of Adsorbed Molecules," Phys. Rev. B 31, 6789 (1985).
- Gadzuk, J. W. and Holloway, S., "On the Dissociation of Diatomic Molecules at Metal Surfaces," Chem. Phys. Lett. 114, 314 (1985).
- Gadzuk, J. W. and Luntz, A. C., "On Vibrational Lineshapes of Adsorbed Molecules," Surf. Sci. 144, 429 (1984).
- Gadzuk, J. W. and Nørskov, J. K., "Vibrational Excitation, Harpooning and Sticking in Molecule-Surface Collisions," J. Chem. Phys. 81, 2828 (1984).
- Girvin, S. M., MacDonald, A. H. and Platzman, P. M., "Collective Excitation Gap in the Quantum Hall Effect," Phys. Rev. Lett. 54, 581 (1985).
- Glick, A. J. and Bryant, G. W., "Effect of Anisotropy on the Optical Absorption Spectrum of Polyacetylene," Phys. Rev. B. 28, 4295 (1983).
- Goodman, D. W. and Yates, Jr., J. T., "CO Isotopic Mixing Measurements in Nickel: Evidence for Irreversibility of CO Dissociation," J. Catalysis 82, 255 (1983).
- Heilweil, E. J., Casassa, M. P. Cavanagh, R. R. and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," in Ultrashort Pulse Spectroscopy and Applications, SPIE Vol. 533 (Society of Photo-Optical Instrumentation Engineers, WA), 15 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenon, J. C., "Picosecond Vibrational Energy Relaxation of Surface Hydroxyl Groups on Colloidal Silica," J. Chem. Phys. 81, 2856 (1984).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenson, J. C., "Temperature Dependence of the Vibrational Population Lifetime of OH($\nu=1$) in Fused Silica," Chem. Phys. Lett. 117, 185 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenson, J. C., "Vibrational Deactivation of Surface OH Chemisorbed on SiO₂: Solvent Effects," J. Chem. Phys. 82, 5216 (1985).
- Heinonen, O., Taylor, P. L. and Girvin, S. M., "Electron-Phonon Interactions and the Breakdown of the Dissipationless Quantum Hall Effect," Phys. Rev. B. 30, 3016 (1984).
- Holloway, S. and Gadzuk, J. W., "Energy Redistribution and Dissociation in Molecule-Surface Collisions Involving Charge Transfer/Surface Hopping," Surf. Sci. 152, 838 (1985).
- Holloway, S. and Gadzuk, J. W., "Charge Transfer, Vibrational Excitation, and Dissociative Adsorption in Molecular-Surface Collisions: Classical Trajectory Theory," J. Chem. Phys. 82, 5203 (1985).

- Kelley, R. D., Cavanagh, R. R., Rush, J. J. and Madey, T. E., "Neutron Spectroscopic Studies of the Adsorption and Decomposition of C_2H_2 and C_2H_4 on Raney Nickel," *Surf. Sci.* 155, 480 (1985).
- King, D. S., Mantell, D. A. and Cavanagh, R. R., "NO Thermally Desorbed From a Saturation Coverage on Pt(111): Internal State Distributions," *J. Chem. Phys.* 82, 1046 (1985).
- Kurtz, R. L., Stockbauer, R. and Madey, T. E., "Site Specificity in Stimulated Desorption from TiO_2 ," in Desorption Induced by Electronic Transitions II, eds. W. Brenig and D. Menzel, Springer Series in Surface Sciences, Vol. 4 (Springer-Verlag, Heidelberg), 89 (1985).
- Landman, U., Kleiman, G. G., Cleveland, C. L., Kuster, E., Barnett, R. N., and Gadzuk, J. W., "Hindered and Modulated Rotations of Adsorbed Diatomic Molecules: States and Spectra," *Phys. Rev. B.* 29, 4313 (1984).
- Madey, T. E., "The Uses and Limitations of ESDIAD for Determining the Structure of Surface Molecules," in The Structure of Surfaces, Springer Series in Surface Science 2, eds. M. A. Van Hove and S. Y. Tong (Springer-Verlag, New York), 264 (1985).
- Madey, T. E. and Benndorf, C., "Influence of Surface Additives (Na and O) on the Adsorption and Structure of NH_3 on Ni(110)," *Surf. Sci.* 152/153, 587 (1985).
- Madey, T. E., Benndorf, C., Shinn, N. D., Miskovic, Z. and Vukanic, J., "Recent Advances using ESDIAD: Applications to Surface Chemistry," in Desorption Induced by Electronic Transitions II, eds. W. Brenig and D. Menzel, Springer Series in Surface Sciences, Vol. 4 (Springer-Verlag, Heidelberg), 104 (1985).
- Madey, T. E., Ramaker, D. E. and Stockbauer, R., "Characterization of Surfaces Using Electron and Photon Stimulated Desorption," *Ann. Rev. Phys. Chem.* 35, 215 (1984).
- Madey, T. E. and Stockbauer, R., "Experimental Methods in Electron and Photon Stimulated Desorption," in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 465 (1985).
- Matthew, J. A. D., "Comparison of Vibrational Broadening in Auger and Photoelectron Spectroscopy," *Phys. Rev. B* 29, 3031 (1984).
- Matthew, J. A. D., "Auger Spectroscopy of Solid Surfaces: Electron Versus Ion Excitation," *Phys. Scripta.* T6, 79 (1983).
- Melmed, A. J. and Carroll, J. J., "An Approach to Realism in Field Ion Microscopy via Zone Electropolishing," *J. Vac. Sci. Tech.* A2, 1388 (1984).
- Melmed, A. J., Maurice, V., Frank, O. and Block, J. H., "Rare-Earth Crystal Growth from the Vapor: Eu/Re and Eu/W," *J. de Physique* 45, C9 (1984).

- Melmed, A. J., Twigg, M. E., Klein, R., Kaufman, M. J. and Fraser, H. L., "The Complementary Use of Atom Probe Field Ion Microscopy and Analytical Transmission Electron Microscopy for the Study of a Ni-Base Superalloy," *J. de Physique* 45, C9 (1984).
- Navinsek, B., Panjan, P., Zabkar, A. and Fine, J., "A Comparison of Sputtered Ni/Cr Interface Depth Resolution as Obtained by the Quartz Crystal Microbalance Mass-Loss Method and Auger Spectroscopy," *J. Vac. Sci. Tech.* A3, 671 (1985).
- Nöbl, C., Benndorf, C. and Madey, T. E., " H_2O Adsorption on Ni(110): Evidence for Oriented Water Dimers," *Surf. Sci.* 157, 29 (1985).
- Penn, D. R., Apell, S. P. and Girvin, S. M., "Theory of Spin-Polarized Secondary Electrons in Transition Metals," *Phys. Rev. Lett.* 55, 518 (1985).
- Powell, C. J., "Inelastic Mean Free Paths and Attenuation Length of Low-Energy Electrons in Solids," *Scanning Electron Microscopy/1984*, 1649 (1984).
- Powell, C. J., "Energy and Material Dependence of the Inelastic Mean Free Path of Low-Energy Electrons in Solids," *J. Vac. Sci. Tech.* A3, 1388 (1985).
- Powell, C. J., "Innershell Ionization Cross Sections," in Electron Impact Ionization, edited by T. D. Märk and G. H. Dunn (Springer-Verlag, New York), 198 (1985).
- Powell, C. J. (editor), "Technical Activities 1984 - Surface Science Division," NBSIR 84-2994 (1985).
- Rendell, R. W. and Girvin, S. M., "Quantum Hall Effect: Role of Inversion Layer Geometry and Random Impurity Potential" in Precision Measurements and Fundamental Constants II, eds. B. N. Taylor and W. D. Phillips, National Bureau of Standards Spec. Publ. 617, 557 (1984).
- Schmidt-May, J., Senf, F., Voss, J., Kunz, C, Flodström, A., Nyholm, R. and Stockbauer, R., "Resonant Photoemission and PSD of Rare Earth Oxides," Desorption Induced by Electronic Transitions II, eds. W. Brenig and D. Menzel, Springer Series in Surface Sciences (Springer-Verlag, Heidelberg), 94 (1985).
- Seah, M. P. and Powell, C. J., "The Coordinated Development of Standards for Surface Chemical Analysis," NBSIR 85-3120 (1985).
- Shinn, N. D. and Madey, T. E., "Unusual C-O Bond Weakening on a Clean Metal Surface: CO on Cr(110)," *Phys. Rev. Lett.* 53, 2481 (1984).
- Shinn, N. D. and Madey, T. E., "Oxygen-Induced CO Reorientation on Cr(110)," *J. Vac. Sci. Tech.* A3, 1673 (1985).
- Twigg, M. E., "The Effect of Bremsstrahlung-Produced Fluorescence in X-Ray Microanalysis in the Analytical Transmission Electron Microscope," *J. Electron Microsc.* 134, 2 (1984).

Twigg, M. E., Melmed, A. J., Klein, R., Kaufman, M. J. and Fraser, H. L., "A Microanalytical Study of Secondary Precipitation in RSR143 using Atom Probe Field Ion Microscopy and Analytical Transmission Electron Microscopy," *Superalloys 631* (1984).

Udovic, T. J., Kelley, R. D. and Madey, T. E., "The Methanation Activity of W(110)," *Surf. Sci.* 150, L71 (1985).

Yates, Jr., J. T., "The Thermal Desorption of Adsorbed Species," in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds, (Academic Press, N.Y.), 425 (1985).

Yates, Jr., J. T. and Haller, G. L., "The Interaction of Physisorbed Species with Chemisorbed Species as Studied by Infrared Spectroscopy," *J. Phys. Chem.* 88,4660 (1984).

(b) Publications in Progress

- Bange, K., Madey, T. E. and Sass, J. K., "The Structure of the Surface Hydration Shell of Bromide on Ag(110)," Surf. Sci. (in press).
- Brennan, S., Cowan, P. L., Jach, T., Lavilla, R., Perera, R. C. C. and Winick, H., "Optical and Spectral Characteristics of an Insertion Device Used Both as a Wiggler and an Undulator," Nucl. Instr. and Meth. (in press).
- Casassa, M. P., Heilweil, E. J., Stephenson, J. C. and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation at Surfaces," J. Elect. Spectroscopy (in press).
- Cavanagh, R. R., Rush, J. J. and Kelley, R. D., "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces" in Vibrational Spectroscopy of Molecules on Surfaces edited by J.T. Yates, Jr. and T. E. Madey, Vol. 4 of Methods of Surface Characterization, Plenum Press Publishing Co., New York, (in press).
- Cowan, P. L., Brennan, S., Deslattes, R. D., Henius, A., Jach, T. and Kessler, E. G., "A High Energy Resolution X-Ray Spectroscopy Synchrotron Radiation Beamline for the Energy Range 800 eV to 5000 eV," Nucl. Instr. and Meth. (accepted).
- Cowan, P. L., Brennan, S., Jach, T., Bedzyk, M. and Materlik, G., "Observations of the Diffraction of Evanescent X-Rays at a Crystal Surface," Phys. Rev. Lett. (submitted).
- Cox, D. F., Semancik, S. and Szuromi, P. D., "Summary Abstract: Structural and Electronic Properties of Clean and Water-Dosed SnO₂ (110)," J. Vac. Sci. Tech. (submitted).
- Egelhoff, Jr., W. F., "Core-Level Binding-Energy Shifts in Solids at Surfaces," Surf. Sci. Reports (submitted).
- Erickson, N. E., "Modified Structural Proposal for the Si(111)-(7x7) Reconstruction Based on an Analysis of Chemisorption Data," Phys. Rev. B. (submitted).
- Erickson, N. E. and Powell, C. J., "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," Surf. Interface Anal. (submitted).
- Erickson, N. E. and Powell, C. J., "Imaging Properties and Energy Aberrations of a Double-Pass Cylindrical-Mirror Electron Energy Analyzer," J. Vac. Sci. Tech. (submitted).
- Gadzuk, J. W., "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces," in Vibrational Spectroscopy of Molecules on Surfaces edited by J. T. Yates, Jr. and T. E. Madey, Vol. 4 of Methods of Surface Characterization, Plenum Press Publishing Co., New York (in press).

- Gadzuk, J. W. and Holloway, S., "Charge Transfer and Vibrational Excitation in Molecule-Surface Collisions: Trajectory-Quantum Theory," *Physica Scripta* (in press).
- Gadzuk, J. W. and Holloway, S., "Collision Induced Dissociation of Diatomic Molecules on Surfaces: A Charge Transfer Mechanism," *J. Chem. Phys.* (in press).
- Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra," *J. Elect. Spectroscopy* (in press).
- Girvin, S. M., MacDonald, A. H. and Platzman, P. M., "Fractional Quantum Hall Effect Superfluidity, Magneto-Rotons, and Fractionally Charged Vortices," *J. of Mag. & Mag. Mat.* (in press).
- Girvin, S. M., MacDonald, A. H. and Platzman, P. M., "Magneto-Roton Theory of Collective Excitations in the Fractional Quantum Hall Effect," *Phys. Rev B* (submitted).
- Karikorpi, M., Holloway, S. and Gadzuk, J. W., "A Classical Trajectory Surface Hopping Approach to Non-Adiabatic Molecule-Surface Processes," *J. Elect. Spectroscopy* (in press).
- King, D. S. and Cavanagh, R. R., "Final-State Resolved Studies of Molecule-Surface Interactions," *New Laser and Optical Investigations of Chemistry and Structures at Interfaces*, Verlag-Chemie (in press).
- Kurtz, R. L., "The Influence of Surface Structure on Ion Emission from TiO_2 ," *J. Vac. Sci. Tech. A* (submitted).
- Kurtz, R. L., Stockbauer, R. and Madey, T. E., "Angular Distributions of Ions Desorbing from TiO_2 ," *Nucl. Instr. & Meth. B.* (submitted).
- Kurtz, R. L., Usuki, N., Stockbauer, R. and Madey, T. E., "Measurements of Electron Attenuation Lengths in Condensed Molecular Solids," *J. Elect. Spect. Rel. Phn.* (submitted).
- Madey, T. E., "Mechanisms and Applications of Electron Stimulated Desorption in Surface Science," *Vacuum* (in press).
- Madey, T. E. and Benndorf, C., "Evidence for Molecular Orientations in Co-adsorption of CO and K on Ru(001)," *Surf. Sci.* (in press).
- Mantell, D. A., Cavanagh, R. R. and King, D. S., "Internal States Distributions of NO Thermally Desorbed from Pt(111): Dependence on Coverage and Co-adsorbed CO," *J. Chem. Phys.* (submitted).
- MacDonald, A. H. and Girvin, S. M., "Collective Excitations of Fractional Hall States in Higher Landau Levels," *Phys. Rev. B. Rapid Commun.* (submitted)
- MacDonald, A. H. and Girvin, S. M., "Quasi-Particle States and the Fractional Quantum Hall Effect," *Phys. Rev. Lett.* (submitted).

- MacDonald, A. H., Liu, K. L. and Girvin, S. M., "Disorder and the Fractional Quantum Hall Effect: Activation Energies and the Collapse of the Gap," Phys. Rev. B. (submitted).
- MacDonald, A. H., Oji, H. C. A. and Girvin, S. M., "Magnetoplasmon Excitations from Partially Filled Landau Levels," Phys. Rev. Lett. (submitted).
- Mišković, Z., Vukanić, J. and Madey, T. E., "Calculations of Reneutralization Effects in ESDIAD," Surf. Sci. (submitted).
- Penn, D. R., Apell, S. P. and Girvin, S. M., "Spin Polarization of Secondary Electrons in Transition Metals: Theory," Phys. Rev. B (submitted).
- Platzman, P. M., Girvin, S. M. and MacDonald, A. H., "Conductivity in the Fractionally Quantized Hall Effect," Phys. Rev. Lett. (submitted).
- Powell, C. J., "Calculations of Electron Inelastic Mean Free Paths from Experimental Optical Data," Surf. Interface Anal. (in press).
- Powell, C. J., "The Energy Dependence of Electron Attenuation Lengths," Surf. Interface Anal. (in press).
- Powell, C. J., "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy," J. Vac. Sci. Tech. (submitted).
- Powell, C. J. and Seah, M. P., "Surface Chemical Analysis-Report on the VAMAS Project," Surf. Interface Anal. (submitted).
- Rush, J. J., Cavanagh, R. R., Kelley, R. D. and Rowe, J. M., "Interaction of Vibrating H Atoms on the Surface of Platinum Particles by Isotope Dilution Neutron Spectroscopy," J. Chem. Phys. (in press).
- Shinn, N. D., "Synchrotron Photoemission Evidence for 'Lying-Down' CO on Cr(110)," J. Vac. Sci. Tech. (submitted).
- Shinn, N. D. and Madey, T. E., "CO Chemisorption on Cr(110): Evidence for a Precursor to Dissociation," J. Chem. Phys. (in press).
- Shinn, N. D. and Madey, T. E., "Observation of a Metal: CO σ Bonding Interaction for Chemisorbed CO on Cr(110)," Phys. Rev. B (submitted).
- Shinn, N. D. and Madey, T. E., "Chemisorption and Dissociation of O₂ on Cr(110): An EELS/ESDIAD Study," Nucl. Instr. & Meth. B. (in press).
- Stockbauer, R., Kurtz, R. L., Usuki, N. and Madey, T. E., "The Use of Synchrotron Radiation to Measure Electron Attenuation Lengths in Condensed Molecular Solids," Nucl. Instr. & Meth. B. (submitted).
- Twigg, M. E., Melmed, A. J., Klein, R., Kaufman, M. J. and Fraser, H. L., "A Microanalytical Study of Secondary Precipitation in a Nickel-Base Superalloy with use of Atom Probe Field Ion Microscopy and Analytical Electron Microscopy," Proc. Fifth Int. Symposium on Superalloys (in press).

- Wang, F. W., Lowry, R. E. and Cavanagh, R. R., "Picosecond Excimer Fluorescence Spectroscopy: Applications to Local Motions of Polymers and Polymerization Monitoring," Polymer (submitted).
- Wax, M. J., Cavanagh, R. R., Rush, J. R., Stucky, G. D., Abrams, L. and Corbin, D. R., "A Neutron Scattering Study of Zeolite Rho," J. Phys. Chem. (submitted).
- Wax, M. J., Kelley, R. D. and Madey, T. E., "Ethane Hydrogenolysis Catalyzed by W(110)," J. Catalysis. (submitted).
- Yates, Jr., J. T., Madey, T. E. and Campuzano, J. C., "The Chemisorption of Carbon Monoxide by the Transition Metals," The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, D. A. King and D. P. Woodruff, eds., Elsevier (in press).

c) Recent Publications of New Staff Members (Burgess and Szuromi)

Burgess, Jr., D. R., Hussla, I., Stair, P. C., Viswanthan, R., and Weitz, E., "Pulsed Laser-Induced Thermal Desorption from Surfaces: Instrumentation and Procedures," Rev. Sci. Instrum. 55, 1771 (1984).

Szuromi, P. D., Engstrom, J. R. and Weinberg, W. H., "The Reaction of Saturated and Unsaturated Hydrocarbons with the (110)-(1x2) and (111) Surfaces of Iridium," J. Chem. Phys. 80, 508 (1984).

Szuromi, P. D., Engstrom, J. R. and Weinberg, W. H., "Adsorption and Reaction of N-Alkanes on the Pt(110)-(1x2) Surface," J. Phys. Chem. 89, 2497 (1985).

Szuromi, P. D. and Weinberg, W. H., "The Adsorption and Reaction of Normal Alkanes on the the Ir(110)-(1x2) Surface," Surf. Sci. 149, 226 (1985).

6. TALKS

- Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemistry, California Institute of Technology, Pasadena, CA, November 26, 1984.
- Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemistry, University of Irvine, Irvine, CA, November 27, 1984.
- Cavanagh, R. R., "Laser Diagnostics of Gas/Surface Interactions," American Institute of Chemical Engineers, San Francisco, CA, November 28, 1984.
- Cavanagh, R. R., "Energy Transfer at Surfaces: Pump-Probe Measurements of Vibrational Relaxation," Department of Chemical Physics, IBM, San Jose, CA, November 29, 1984.
- Cavanagh, R. R., "Picosecond Pump-Probe Measurements of Vibrational Relaxation at Surfaces," Department of Chemistry, Rutgers University, Piscataway, NJ, April 1, 1985.
- Cavanagh, R. R., "Energy Transfer at Surfaces: Laser Based Measurements," Local Section of American Vacuum Society, University of Minnesota, Minneapolis, MN, May 16, 1985.
- Cavanagh, R. R., "Energy Transfer at Surfaces: Laser Based Measurements," Physical Chemistry Department, General Motors Company, Detroit, MI, May 24, 1985.
- Cavanagh, R. R., "Nitric Oxide Thermally Desorbed from Pt(111): A Microscopic Test of Transition State Theory," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.
- Cavanagh, R. R., "Hydrogen on Small Metal Particles: Structure and Dynamics from Neutron Scattering," Gordon Research Conference on Metal Hydrides, Tilton, NH, July 15, 1985.
- Cavanagh, R. R., "Vibrational Relaxation at Surfaces: Time Resolved Results," Gordon Research Conference on the Dynamics of Gas-Surface Interactions, New London, NH, July 29, 1985.
- Cavanagh, R. R., "Picosecond Pump Measurements of Vibrational Relaxation at Surfaces," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 17, 1985.
- Cavanagh, R. R., "Inelastic Incoherent Neutron Scattering: Vibrational Spectroscopy of Hydrogen on Platinum Black," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 18, 1985.
- Egelhoff, W. F., Jr., "X-Ray Photoelectron Forward Scattering: A New Tool for Studying Epitaxy and Interfaces," Materials Research Society Meeting, Boston, MA, November 29, 1984.

- Egelhoff, W. F., Jr., "Heats of Adsorption of H and O on Cu-Ni Alloy Surfaces from XPS Data," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.
- Egelhoff, W. F., Jr., "Role of Forward Scattering in Angular Dependent XPS," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.
- Egelhoff, W. F., Jr., "New Applications for Angle Resolved XPS," American Vacuum Society Chapter Meeting, Tampa, FL, February 6, 1985.
- Egelhoff, W. F. Jr., "The XPS Searchlight Effect: A New Analytical Tool for Layered Structure, Epitaxy and Interfaces," American Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 25, 1985.
- Egelhoff, W. F. Jr., "A Core-Level Binding-Energy Shift Analysis of CO, H, and O Adsorption on Cu-Ni Surfaces," American Physical Society Meeting, Baltimore, MD, March 28, 1985.
- Egelhoff, W. F., Jr., "Forward Scattering in XPS: A Structural Tool for Surfaces, Interfaces and Epitaxy," Chemistry Department, University of California, Berkeley, CA, April 25, 1985.
- Egelhoff, W. F., Jr., "Forward Scattering in XPS: A Structural Tool for Surfaces, Interfaces and Epitaxy," Applied Physics Department, Stanford University, Stanford, CA, April 26, 1985.
- Erickson, N. E., "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," 6th Symposium on Applied Surface Analysis, University of Maryland, College Park, MD, May 15, 1985.
- Fine, J., "Ion-Beam Mixing and Radiation-Induced Segregation During Sputter Profiling of Nickel/Silver Interfaces," Condensed Matter and Radiation Sciences Division Seminar, Naval Research Laboratory, Washington, D.C., November 1, 1984.
- Fine, J., "Characterization of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," 31st National Symposium of the American Vacuum Society, Reno, NV, December 4, 1984.
- Fine, J., "A Comparison of Sputtered Ni/Cr Interface Depth Resolution as Obtained by the Quartz Crystal Microbalance Mass-Loss Method and Auger Spectroscopy," 31st National Symposium of the American Vacuum Society, Reno, NV, December 5, 1984.
- Fine, J., "Interface Depth Resolution of Auger Sputter Profiled Ni/Cr Interfaces: Dependence on Ion Beam Parameters," 31st National Symposium of the American Vacuum Society, Reno, NV, December 7, 1984.
- Fine, J., "Sputter Profile Shapes and Widths of Ni/Cr Interfaces: Their Dependence on Ion Bombardment Parameters," Seventh International Conference on Ion Beam Analysis, Hahn Meitner Institute, Berlin, W. Germany, July 9, 1985.

- Gadzuk, J. W., "Molecular Scattering, Energy Redistribution, and Dissociative Adsorption at Surfaces," Surface Science Seminar, Imperial College, London, England, September 24, 1984.
- Gadzuk, J. W., "Intra-Molecular Wavepacket Dynamics in Molecule-Surface Scattering," Workshop on Interactions of Molecular Beams with Solid Surfaces, St. John's College, Cambridge, England, September 27, 1984.
- Gadzuk, J. W., "Vibrational Lineshapes of Adsorbed Molecules," Department of Physical Chemistry Seminar, University of Liverpool, Liverpool, England, October 1, 1984.
- Gadzuk, J. W., "Dynamic Effects in Electronic Excitation and Molecular Scattering from Surfaces," Department de Medecine Nucleaire and Radiobiologie, Centre Hospitalie-Universitaire, Sherbrooke, Quebec, Canada, January 21, 1985.
- Gadzuk, J. W., "Recent Advances in Vibrational Spectroscopy at Surfaces," Department de Medecine Nucleaire and Radiobiologie, Centre Hospitalie-Universitaire, Sherbrooke, Quebec, Canada, January 22, 1985.
- Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Physics Department Colloquium, University of Waterloo, Waterloo, Ontario, Canada, January 25, 1985.
- Gadzuk, J. W., "Dissociation Dynamics in Molecule-Surface Collisions," American Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 25, 1985.
- Gadzuk, J. W., "Collision Induced Dissociation of Diatomic Molecules on Surfaces," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.
- Gadzuk, J. W., "A Classical Trajectory Surface Hopping Approach to Non-Adiabatic Processes Occurring During Diatom-Surface Scattering," 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird Resort, Snowbird, UT, July 16, 1985.
- Gadzuk, J. W., "A Trajectorized Quantum Model for Surface Harpooning Processes Occurring in Diatom-Surface Scattering," 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird Resort, Snowbird, UT, July 17, 1985.
- Gadzuk, J. W., "The Vibrational Lineshapes of Adsorbed Molecules," Vibrations at Surfaces IV Conference, Bowness-on-Windermere, England, September 17, 1985.
- Girvin, S. M., "Collective Excitation Gap in the Fractional Quantum Hall Effect," AT&T Bell Laboratory, Murray Hill, NJ, October 31, 1984.
- Girvin, S. M., "The Quantum Hall Effect," Solid State Theory Seminar, Oak Ridge National Laboratory, Oak Ridge, TN, November 2, 1984.

- Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Center for Basic Standards Colloquium, National Bureau of Standards, Gaithersburg, MD, January 9, 1985.
- Girvin, S. M., "Introduction to the Quantum Hall Effect," James Franck Institute Colloquium, University of Chicago, Chicago, IL, January 15, 1985.
- Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Department of Physics, University of Chicago, Chicago, IL, January 16, 1985.
- Girvin, S. M., "The Quantum Hall Effect," Department of Physics, Catholic University, Washington, D.C., February 21, 1985.
- Girvin, S. M., "Rotons in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, Princeton University, Princeton, NJ, March 6, 1985.
- Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, March 11, 1985.
- Girvin, S. M., "Collective Excitation Gap in the Fractional Quantum Hall Effect," American Physical Society Meeting, Baltimore Convention Center Baltimore, MD, March 26, 1985.
- Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, SUNY, Stony Brook, NY, April 26, 1985.
- Girvin, S. M., "Rotons and Vortices in Superfluid Helium and the Fractional Quantum Hall Effect," Physics Department, University of Minnesota, Minneapolis, MN, May 6, 1985.
- Girvin, S. M., "Introduction to the Quantum Hall Effect with Applications to GaAs Heterostructures," Center for Microelectronics and Information Science, University of Minnesota, Minneapolis, MN, May 7, 1985.
- Girvin, S. M., "Rotons, Vortices and Superfluidity in the Fractional Quantum Hall Effect," Institute of Theoretical Physics, University of California, Santa Barbara, CA, June 4, 1985.
- Girvin, S. M., "Introduction to the Quantum Hall Effect," Department of Materials Science, Harry Diamond Laboratories, Adelphi, MD, August 12, 1985.
- Girvin, S. M., "Fractional Quantum Hall Effect: Superfluidity, Magneto-Rotons and Fractionally Charged Vortices," International Conference on Magnetism and Magnetic Materials, San Francisco, CA, August 30, 1985.
- Girvin, S. M., "Introduction to the Quantum Hall Effect," Physics Department, Texas A&M University, September 26, 1985.

- Jach, T., "Observations of Dynamical X-Ray Diffraction from a Crystal Surface at Glancing Incidence," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 26, 1985.
- Jach, T., "Dynamical X-Ray Diffraction at Glancing Incidence: A New Tool for Surface Science," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 18, 1985.
- Kelley, R. D., "Catalytic Activity of Single Crystal Tungsten and Tungsten Carbide Surfaces," Symposium on Advances in Catalytic Chemistry III", Hotel Utah, Salt Lake City, UT, May 22, 1985.
- Kurtz, R. L., "Site Specificity in Stimulated Desorption from TiO_2 ," 2nd International Workshop on Desorption Induced by Electronic Transitions, Elmau, Germany, October 15, 1984.
- Kurtz, R. L., "Surface Studies of the Oxides of Titanium: Electronic Structure, Chemisorption, and Desorption from Ti_2O_3 and TiO_2 ," IBM Thomas J. Watson Research Laboratories, Yorktown Heights, NY, November 8, 1984.
- Kurtz, R. L., "Surface Studies of the Oxides of Titanium: Electronic Structure, Chemisorption and Desorption from Ti_2O_3 and TiO_2 ," Applied Physics Division, Harry Diamond Laboratories, Adelphi, MD, November 20, 1984.
- Kurtz, R. L., "Site Specificity in Stimulated Desorption from TiO_2 ," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 6, 1984.
- Kurtz, R. L., "Influence of Local Environment in Stimulated Desorption from TiO_2 ," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 27, 1985.
- Kurtz, R. L., "Application of Surface Analytical Techniques to the Characterization of Adsorption and Desorption from Solids," Physics Department Colloquium, Brandeis University, Waltham, MA, April 30, 1985.
- Kurtz, R. L., "Surface Science Applications of Residual Gas Analyzers," Residual Gas Analyzer Calibration Workshop, National Bureau of Standards, Gaithersburg, MD, May 7, 1985.
- Madey, T. E., "Uses and Limitations of ESDIAD for Determining the Structures of Surface Molecules," 2nd International Workshop on Desorption Induced by Electronic Transitions, Garmisch, W. Germany, October 16, 1984.
- Madey, T. E., "Desorption Induced by Electronic Transitions," Pittsburgh Surface Science Center Symposium, University of Pittsburgh, Pittsburgh, PA, October 30, 1984.
- Madey, T. E., "Use of ESDIAD in Surface Chemistry," Department of Chemistry, Iowa State University, Ames, IA, November 27, 1984.

- Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," 1985 Symposium on Surface Science (3S'85), Bundessportschule Obertraun, Obertraun, Austria, January 29, 1985.
- Madey, T. E., "Early Applications of Vacuum, From Aristotle to Langmuir," National Bureau of Standards Colloquium, Gaithersburg, MD, February 8, 1985.
- Madey, T. E., "The Structures of Molecules on Surfaces as Determined Using Electron Stimulated Desorption," Department of Chemistry, University of Montreal, Montreal, Canada, February 27, 1985.
- Madey, T. E., "The Structures of Molecules on Surfaces as Determined Using Electron Stimulated Desorption," Department of Chemistry, Howard University, March 8, 1985.
- Madey, T. E., "Characterization of Surfaces Using Electron Stimulated Desorption," Ceremonial Symposium Honoring the Retirement of Homer Hagstrum, AT&T Bell Laboratories, Murray Hill, NJ, March 22, 1985.
- Madey, T. E., "Evidence for Molecular Reorientations in Coadsorption of CO and K on Ru(001)," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 28, 1985.
- Madey, T. E., "Adsorption and Orientation of NH₃ on Clean and Modified Fe(100)," 7th European Conference on Surface Science, Aix-en-Provence, France, April 3, 1985.
- Madey, T. E., "Mechanisms and Applications of Electron Stimulated Desorption," Department of Physics, Vanderbilt University, Nashville, TN, April 26, 1985.
- Madey, T. E., "Electron and Photon Stimulated Desorption of Adsorbed Metals: An Overview," Department of Physics, Vanderbilt University, Nashville, TN, June 21, 1985.
- Madey, T. E., "The Structure and Chemistry of H₂O on Silver Surfaces," Department of Chemistry, Iowa State University, Ames, IA, June 26, 1985.
- Madey, T. E., "Influence of Surface Additive Atoms on the Structure and Chemistry of H₂O on Ag(110)," American Chemical Society Meeting, Americana Congress Hotel, Chicago, IL, September 9, 1985.
- Melmed, A. J., "Long-Range Orientational Order and Icosahedral Symmetry in a Metallic Phase Observed by Field Ion Microscopy," American Physical Society, Baltimore Convention Center, Baltimore, MD, March 28, 1985.
- Melmed, A. J., "Field Emission Microscopy-Trends and Perspectives," 3rd International Field Emission Symposium, Wheeling, W.Va., July 17, 1985.
- Melmed, A. J., "Field Emission Microscopy-Trends and Perspectives," Seventh International Summer Institute in Surface Science, University of Wisconsin, Milwaukee, WI, July 23, 1985.

- Powell, C. J., "Energy and Material Dependence of the Inelastic Mean Free Path of Low-Energy Electrons in Solids," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 6, 1984.
- Powell, C. J., "Physics--What Physicists Do," Career Awareness Day, Walt Whitman High School, Bethesda, MD, December 10, 1984.
- Powell, C. J., "Techniques for Surface Analysis," Analytical Topical Group of the New York Section of the American Chemical Society, New York, NY, April 4, 1985.
- Powell, C. J., "Developments in Quantitative Surface Analysis by Electron Spectroscopy," Eastern Electron Spectroscopy Society Mtg., General Electric R&D Center, Schenectady, NY, June 7, 1985.
- Powell, C. J., "Chemical Bonding Studies at the Solid/Gas Interface with Techniques Using Detected Electrons," Fifth Internat. Conf. on Surface and Colloid Science and 59th Colloid and Surface Science Symposium, Clarkson University, Potsdam, NY, June 25, 1985.
- Shinn, N. D., "Oxygen-Induced CO Reorientation on Cr(110)," 31st National Symposium of the American Vacuum Society, MGM Grand Hotel, Reno, NV, December 7, 1984.
- Shinn, N. D., "Chemisorption on Cr(110): Uncommon Results for O₂ and CO," Surface Physics Group, Sandia National Laboratory, Livermore, CA, December 10, 1984.
- Shinn, N. D., "Recent Results and Realistic Goals of Silicon-Fluorine Chemisorption Studies," Surface Physics Group, Hughes Research Laboratory, Malibu, CA, December 12, 1984.
- Shinn, N. D., "Novel O₂ and CO Chemisorption on Cr(110) as Revealed by Stimulated Desorption and Surface Spectroscopies," Los Alamos National Laboratory, Los Alamos, NM, March 12, 1985.
- Shinn, N. D., "CO Chemistry on the Cr(110) Surface: Insights from Unexpected Results," Sandia National Laboratory, Albuquerque, NM, March 14, 1985.
- Shinn, N. D., "A Molecular Precursor to CO Dissociation on Cr(110): The α_1 CO Binding Mode," Americal Physical Society Meeting, Baltimore Convention Center, Baltimore, MD, March 27, 1985.
- Shinn, N. D., "Synchrotron Photoemission Study of Chemisorbed α_1 CO and α_2 CO on Cr(110)," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 17, 1985.
- Shinn, N. D., "CO:O₂ Interactions on Cr(110): Insights into Surface Poisoning by Electronegative Adatoms," Department of Physics, Cornell University, Ithaca, NY, August 14, 1985.
- Stockbauer, R., "Photon and Electron Stimulated Desorption of Ions from Surfaces: Mechanisms and Applications," Physics Department Colloquium, University of Nebraska, Lincoln, NE, April 4, 1985.

Stockbauer, R., "Photon and Electron Stimulated Desorption of Ions from Surfaces: Mechanisms and Applications," Rice University, Houston, TX, June 1985.

Stockbauer, R., "The Use of Synchrotron Radiation to Measure Electron Attenuation Lengths in Condensed Molecular Solids," Synchrotron Radiation Instrumentation Conference, Stanford University Conference Center, Stanford, CA, August 1, 1985.

Szuromi, P. D., "UHV Studies of Alkane Activation on Iridium and Platinum Surfaces," Department of Physics and Astronomy, University of Maryland, College Park, MD, February 1, 1985.

Szuromi, P. D., "Site Specificity of Dissociative Alkane Adsorption on Platinum and Iridium Surfaces," Physical Electronics Conference, University of Wisconsin, Milwaukee, WI, June 18, 1985.

Szuromi, P. D., "The Effect of Adsorbed Sulfur on the Hydrogenation of CO over W(110)" American Chemical Society Meeting, Americana Congress Hotel, Chicago, IL, September 10, 1985.

Szuromi, P. D., "Comparative Studies of Alkane Activation by Low Index Surfaces of Platinum and Iridium," American Chemical Society, Americana Congress Hotel, Chicago, IL, September 10, 1985.

Twigg, M. E., "An Atom Probe Study of Superalloy Microstructure," 5th Annual Symposium on Superalloys, Seven Springs Mountain Resort, Champion, PA, October 9, 1984.

Wax, M. J., "Neutron Scattering Studies of Zeolite Rho," 189th National Meeting of the American Chemical Society, Miami Beach Convention Center, Miami, FL, April 29, 1985.

Wax, M. J., "Thin Platinum Films as Model Alkane Reforming Catalysts," 189th National Meeting of the American Chemical Society, Eden Roc Hotel, Miami, FL, May 2, 1985.

Wax, M. J., "Thin Platinum Films as Model Alkane Reforming Catalysts," Symposium on Applied Surface Analysis, University of Maryland, College Park, MD, May 16, 1985.

Wax, M. J., "Reforming Reactions of Ultrathin Film Model Catalysts," American Chemical Society, Chicago, IL, September 10, 1985.

7. SEMINARS

- Bennett, J. M., Naval Weapons Center, China Lake, CA, "Optical Evaluation Techniques for Films and Surfaces," November 21, 1984.
- Bishop, H. E., Materials Development Division, AERE Harwell, England, "Electron Channeling Effects in Auger Electron Spectroscopy and Secondary Electron Emission," September 26, 1985.
- Cavanagh, R. R., National Bureau of Standards, Gaithersburg, MD, "Temporal and Spectral Probes of Surface Processes: New Opportunities with Laser Diagnostics," May 21, 1985.
- Egelhoff, W. F., Jr., National Bureau of Standards, Gaithersburg, MD, "The XPS Searchlight Effect: A New Analytical Tool for Layered Structures, Epitaxy, and Interfaces," February 11, 1985.
- Einstein, T., University of Maryland, College Park, MD, "How and Why to Study Critical Properties of Surfaces and Adsorbates," October 11, 1984.
- Ekaradt, W., Fritz Haber Institute, Berlin, W. Germany, "Size Dependent Photoabsorption and Photoemission From Small Metal Particles," April 18, 1985.
- Flodström, A., Lund University, Lund, Sweden, "Angle Resolved Photoemission Studies of Semiconductor Surfaces: Mostly Silicon and Germanium," June 13, 1985.
- Freeman, R., AT&T Bell Laboratories, Murray Hill, NJ, "Picosecond Time Resolved Photoemission from Surfaces of Semiconductors," (cosponsored with NBS Radiation Physics Division) January 31, 1985.
- Gurney, B. A., Cornell University, Ithaca, NY, "Adsorption and Desorption of CO on Ni(110)," December 17, 1985.
- Heiland, W., Vanderbilt University, Nashville, TN, "Polarized Light Emission from Grazing Incidence He + Ni(111) Interactions," September 18, 1985.
- Hicks, R., WR Grace & Company, Columbia, MD, "The Effects of Metal-Support Interactions on Palladium: Methanol Synthesis Catalysts," April 25, 1985.
- Israelachvili, J. N., Australian National University, Canberra, Australia, "Forces Between Surfaces," (cosponsored with NBS Inorganic Materials and Thermophysics Divisions) July 1, 1985.
- Johnson, A. L., University of California, Berkeley, CA, "Orientation of Molecules by NEXAFS (Near Edge X-Ray Absorption Fine Structure)," April 12, 1985.
- Karikorpi, M., University of Liverpool, Liverpool, England, "Interaction of H₂ with Metal Surfaces: Dynamics," July 10, 1985.

- Klein, R., National Bureau of Standards, Gaithersburg, MD, "Weighty Considerations on the Micro-Mass-Analysis of Alloys with the Atom Probe," April 19, 1985.
- Kurtz, R. L., National Bureau of Standards, Gaithersburg, MD, "Implications of Recent Results on Photon-Stimulated Desorption," November 15, 1984.
- McKay, J. M., Yale University, New Haven, CT, "Electronic Structure of NiO-CO, O₂, and H₂O Surface Interactions," June 12, 1985.
- Myers, H. P., Chambers University of Technology, Goteborg, Sweden, "Mixed Valence in Sm Overlayers on Al(001) and Cu(001) Surfaces," January 14, 1985.
- Paal, Z., Hungarian Academy of Sciences, Budapest, Hungary, "Activity, Surface Structure and Composition of Pt-Black," September 19, 1984.
- Pearlstine, K., Harvard University, Cambridge, MA, "Hydrocarbon Chemistry on Modified Tungsten Surfaces: C-H and C-C Bond Activation," March 4, 1985.
- Renouprez, A., Institut de Recherches sur la Catalyse, Villeurbanne Cedex, France, "EXAFS Study of the Structure of Pd Microaggregates. A Combined EXAFS and Neutron Study of Hydride Formation," July 23, 1985.
- Rys, F., Fritz Haber Institute, Berlin, W. Germany, "Surface Roughening and Small-Particle Faceting-With Epitaxial Overtones," April 2, 1985.
- Sass, J., Fritz Haber Institute, Berlin, W. Germany, "Surface Science Model Studies of the Electrochemical Interface," January 17, 1985.
- Sawatzky, G., University of Groningen, Groningen, The Netherlands, "The Electronic Structure, Bandgap, and Spectroscopic Properties of Transition Metal Compounds," (cosponsored with Electron Physics Group) August 20, 1985.
- Schwalke, U., California Institute of Technology, Pasadena, CA, "Vibrational Spectra of Chemisorbed NO₂ and Condensed N₂O₄ on the Ru(001) Surface," July 26, 1985.
- Seah, M., National Physical Laboratory, Teddington, Middlesex, England, "Electron Spectrometer Intensity Transmission Functions for ESCA," November 29, 1984.
- Steigerwald, D., Carnegie-Mellon University, Pittsburgh, PA, "Surface Segregation in NiAu Alloys," March 20, 1985.
- Stockbauer, R., National Bureau of Standards, Gaithersburg, MD, "Studies of Electron Transport and Radiation Damage in Condensed Molecular Films Using Synchrotron Radiation," February 14, 1985.
- Strasser, G., University of Maine, Orono, ME, "Nitrogen Adsorption on Fe(111) from the Extrinsic Precursor to Atomic Nitrogen," September 16, 1985.

Szurumi, P. D., National Bureau of Standards, Gaithersburg, MD, "Alkane Activation of Low Index Surfaces of Iridium and Platinum: Comparative Studies," March 13, 1985.

Szymonski, M., Jagellonian University, Krakow, Poland, "Electron Stimulated Desorption of Neutrals from Alkali Halide Surfaces," January 16, 1985.

Tomanek, D., Free University of Berlin, Berlin, Germany, "Calculation of Potential Energy Surfaces for CO and N₂ Dissociation on Transition Metals," May 28, 1985.

Trenary, M., University of Illinois, Chicago, IL, "Infrared Reflection-Absorption Spectroscopy of CO on Clean and Sulfided Ni(111)," November 28, 1984.

Yarmoff, J., University of California, Los Angeles, CA, "Low Energy Ion Backscattering Spectroscopies Applied to the Determination of Surface Structure," March 20, 1985.

8. TECHNICAL AND PROFESSIONAL COMMITTEE
PARTICIPATION AND LEADERSHIP

Cavanagh, R. R.

Surface Science Division Safety Officer

Treasurer, General Committee of the Physical Electronics Conference
(from 7/85)

Erickson, N. E.

Member, ASTM Committee E-42 on Surface Analysis

Fine, J.

Chairman, Subcommittee E-42.09 on Standard Reference Materials of ASTM
Committee E-42 on Surface Analysis

Member, Program Committee, 11th Conference on Atomic Collisions in
Solids, Washington, D.C., August, 1985.

Gadzuk, J. W.

Treasurer, General Committee of the Physical Electronics Conference
(through 6/85)

Member, Editorial Advisory Board, "Progress in Surface Science"

Kelley, R. D.

Chairman, Subcommittee D-32.03 on Chemical Analysis of ASTM Committee
D-32 on Catalysts

Madey, T. E.

Member, Executive Committee of the Governing Board of the American
Institute of Physics (through 3/85); member of AIP Committee on
Corporate Associates, and member of AIP Subcommittee on Electronic
Publishing

U.S. Representative to Surface Science Division of the International
Union of Vacuum Science, Technique and Applications (IUVSTA) and
Secretary of Committee

Member, International Advisory Committee, Second International Conference
on the Structure of Surfaces, Amsterdam, The Netherlands, June, 1987

Program Chairman, International Vacuum Congress and International
Conference on Solid Surfaces, Baltimore, MD, October, 1986

Member, Organizing Committee, 11th Conference on Atomic Collisions in
Solids, Washington, D.C., August, 1985

Member, International Advisory Committee, Second Workshop on Desorption
Induced by Electronic Transitions, Garmisch, W. Germany, October, 1984

Member, Program Advisory Committee for the Synchrotron Radiation Center
of the University of Wisconsin, Madison, Wisconsin

Member, Advisory Committee for Laboratory of Surface Science and Technology at the University of Maine, Orono, ME

Member, Davisson-Germer Prize Committee of the American Physical Society

Chairman, Committee for Foreign Interactions, American Vacuum Society

Co-Editor, "History of Vacuum Science and Technology", a monograph to commemorate the 30th Anniversary of the American Vacuum Society (published 11/84)

Member, ASTM Committee E-42 on Surface Analysis

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of two volumes in series

Member, Editorial Board, "Journal of Vacuum Science and Technology"

Melmed, A. J.

Secretary, Steering Committee, International Field Emission Symposium

Powell, C. J.

Chairman, ASTM Committee E-42 on Surface Analysis

Chairman, Surface Chemical Analysis Working Party, Versailles Project on Advanced Materials and Standards

Member, Board of Trustees, Gordon Research Conferences; Vice-Chairman of Board and Chairman of Selection and Scheduling Committee

Chairman, American Vacuum Society Surface Science Division (through 11/84)

Trustee, American Vacuum Society Scholarships and Awards Committee

Instructor, American Vacuum Society Short Course: "Surface Analysis by Electron Spectroscopy"

Chairman, Study Group to Examine AVS-ASTM E-42 Interactions

Chairman, Local Committee, Meeting of American Physical Society, Baltimore, MD, March 1985

Member, Editorial Board, "Applications of Surface Science"

Member, Editorial Board, "Surface and Interface Analysis"

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of one volume in series

Stockbauer, R.

Assistant Program Chairman, International Vacuum Congress and International Conference on Solid Surface, Baltimore, MD, October, 1986.

9. PROFESSIONAL INTERACTIONS, CONSULTING
AND ADVISORY SERVICES

Cavanagh, R.R.

Collaborating with Dr. D. S. King of the NBS Molecular Spectroscopy Division on state-specific diagnostics of molecular desorption processes

Collaborating with Drs. M. P. Casassa, E. J. Heilweil and J. C. Stephenson of the NBS Molecular Spectroscopy Division on real time measurements of vibrational relaxation processes at surfaces

Collaborating (with R. D. Kelley and M. J. Wax) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbates on high-surface-area transition metals

Collaborating with Dr. J. J. Rush of the NBS Reactor Radiation Division, Dr. G. D. Stucky of du Pont, and Dr. M. J. Wax on vibration and diffusion properties of hydrogen and ammonia in zeolite H-rho

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division and Dr. B. J. Tatarchuk of Auburn University on neutron inelastic scattering measurements from adsorbates on dispersed ruthenium catalysts

Egelhoff, Jr., W. F.

Collaborating with Dr. R. A. Armstrong of the National Research Council, Ottawa on a theoretical analysis of the basic physics of the XPS searchlight effect for the purpose of defining and extending its range of applicability as an analytical tool for surfaces and interfaces.

Fine, J.

Collaborating with Prof. B. Navinsek of the J. Stefan Institute, Ljubljana, Yugoslavia on the effect of surface topography on measurements of sputtering yields, on depth resolution at interfaces, and on the fabrication and characterization of standard reference materials for surface analysis. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. I. Terzic of the Boris Kidric Institute, Belgrade, Yugoslavia on electronic excitation and electron emission for ion-bombarded surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Drs. L. and N. Tanovic of the University of Sarajevo, Yugoslavia on characterizing surface topography changes that result from ion bombardment. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. T. Nevadovic of the Boris Kidric Institute, Belgrade, Yugoslavia on the surface-topography effect of both particle and laser-beam interactions with thin solid films. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. L. J. Moore of the NBS Inorganic Analytical Research Division and Dr. T. Lucatorto of the NBS Radiation Physics Division on the use of laser multiphoton ionization techniques to identify sputtered atoms and to determine their kinetic energies.

Collaborating with Dr. W. Kirchhoff of the NBS Chemical Thermodynamics Division on a data analysis procedure for sputter-depth-profile interface characterization.

Collaborating with Dr. R. F. Fleming of the NBS Inorganic Analytical Research Division on thin-film thickness measurements of standard reference materials for surface analysis.

Collaborating with Dr. P. A. Lindfors of the Physical Electronics Division of Perkin-Elmer Corp. on the interface depth resolution of sputter-profiled Ni/Cr interfaces.

Collaborating with Drs. C. Le Gressus and J. P. Duraud of the Centre d'Etudes Nucleaires de Saclay, France on the collisional excitation and electron decay of atoms at single-crystal surfaces.

Gadzuk, J. W.

Collaborating with Prof. M. Sunjic of the Rudnor Boskovic Institute and the University of Zagreb, Yugoslavia on theories of electron spectroscopies and dynamics of molecular processes at surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Prof. U. Landman of the Georgia Institute of Technology on theoretical modeling of non-linear and stochastic molecular processes at surfaces.

Collaborating with Dr. S. Holloway and Ms. M. Karikorpi, University of Liverpool, England on classical trajectory theories of molecular processes at surfaces. This collaboration is assisted by a grant from the NATO Scientific Affairs Division.

Collaborating with Dr. E. Hood, California Institute of Technology, on a theory of polarized-metastable-helium de-excitation spectroscopy at magnetic surfaces and on electron-transfer probabilities.

Invited lecturer and participant at the Fourth Electrochemistry Study Group, Fritz-Haber-Institute, Berlin, September 22-27, 1985.

Girvin, S. M.

Collaborating with Drs. A. H. McDonald of the National Research Council of Canada, Ottawa and P. M. Platzman of AT&T Bell Laboratories, Murray Hill on developing a new theory of collective excitations in the fractional quantum Hall effect.

Collaborating with Dr. M. Jonson of Chalmers University of Technology, Gothenburg, Sweden on the theory of the thermoelectric effect in disordered quantum Hall systems.

Collaborating with Drs. D. R. Penn and S. P. Apell of the NBS Radiation Physics Division on a theory of spin polarization in secondary cascades in ferromagnets.

Collaborating with Prof. R. E. Prange of the University of Maryland in the organization of a lecture series on the quantum Hall effect during fall, 1985. It is planned to publish the lectures as a book.

Visited the Institute of Theoretical Physics at Santa Barbara during June 3-8, 1985 at the invitation of Prof. J. R. Schrieffer.

Visited AT&T Bell Laboratories, Murray Hill during July 2-12, 1985 at the invitation of Dr. D. S. Fisher.

Jach, T. J.

Collaborating with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group on the development of a beamline at the National Synchrotron Light Source, Brookhaven and on experiments to study electronic effects associated with core-level ionization in atoms, molecules, and solids.

Collaborating with Drs. P. Cowan and S. Brennan of the NBS Quantum Metrology Group and with Drs. G. Materlik and M. Bedzik of the German Electron Synchrotron Laboratory DESY, Hamburg on surface and interface x-ray diffraction experiments at DESY using glancing incidence.

Collaborating with Drs. G. G. Hembree of the NBS Mechanical Production Metrology Division and L. B. Holdeman of COMSAT on the fabrication and characterization of ultra-smooth surfaces and thin films.

Collaborating with Dr. P. Cowan of the NBS Quantum Metrology Group on glancing incidence x-ray excitation of surface atoms to measure surface core-level binding-energy shifts.

Collaborating with Dr. R. Perera of Lawrence Berkeley Laboratory on an experiment to measure Auger-electron spectra of argon for near-threshold excitation at the Stanford Synchrotron Radiation Laboratory.

Collaborated with Dr. H. Winick of the Stanford Synchrotron Radiation Laboratory to improve undulator efficiency.

Kelley, R. D.

Collaborating (with R. R. Cavanagh and M. J. Wax) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Division on neutron inelastic scattering measurements of adsorbates on optically opaque high-surface-area transition metals.

Working on detail as a Program Manager with the Department of Energy Office of Energy Research, Division of Chemical Sciences. This detail is on a 70% part-time basis for a two-year period beginning May, 1985.

Kurtz, R. L.

Collaborating with Prof. V. E. Henrich of Yale University on studies of the chemisorption of molecules of catalytic interest on transition-metal oxide surfaces.

Collaborating (with R. Stockbauer) with Drs. C. Kunz and J. Schmidt-May of the German Synchrotron Laboratory DESY, Hamburg and Dr. A. Flodström of Lund University, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. Stockbauer) with Dr. A. Flodström of Lund University, Sweden on experiments at the NBS synchrotron radiation facility of SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) angular distributions (ESDIAD) of ions desorbing from adsorbates on semiconductors.

Collaborating (with R. Stockbauer) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with T. E. Madey and R. Stockbauer) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with R. Stockbauer) with Mr. J. Jimenez of Yale University, Prof. D. Caldwell of the University of Florida, and Dr. D. L. Ederer of the NBS Radiation Physics Division on measurements of the angular distribution of fluorescence from molecules excited by synchrotron radiation from the NBS SURF-II facility.

Collaborating with Dr. J. Pena of the University of Mexico, Mexico City on the preparation of TiO_2 samples suitable both for photon-stimulated desorption experiments at NBS and for secondary-ion mass spectroscopy experiments in Mexico.

Madey, T. E.

Collaborating with Drs. I. Terzić, J. Vukanić and Z. Mišković of the Boris Kidrić Institute, Belgrade, under the auspices of the U.S.-Yugoslav Agreement for Cooperation in Science and Technology, on theoretical and experimental studies of electron-stimulated desorption and scattering of alkali ions from surfaces.

Collaborating (with R. L. Kurtz and R. Stockbauer) with Drs. W. R. Hunter, J. Rife and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating with Drs. J. Sass and K. Bange of the Fritz-Haber-Institute, Berlin, and with Dr. E. Stuve of the University of Washington on fundamental studies of electrochemical phenomena with emphasis on the interaction between water and surfaces.

Collaborating with Dr. N. Tolk of Vanderbilt University on studies of electron-stimulated desorption of excited-alkali neutral atoms from surfaces.

Collaborating with Dr. C. Benndorf of the University of Hamburg, under the auspices of a NATO grant, on studies of the influence of surface additives on local molecular structure.

Collaborating with Prof. P. A. Thiel of the Dept. of Chemistry, Iowa State University in writing a comprehensive review article on the interaction of water with solid surfaces.

Melmed, A. J.

Collaborating as a co-principal investigator with Prof. W. R. Graham of the University of Pennsylvania on studies of atomic reconstruction of metal and semiconductor surfaces.

Collaborating with Dr. W. A. Schmidt and Prof. J. H. Block of the Fritz-Haber-Institute, Berlin on properties of semiconductors in electric fields and effects due to metallic overlayers.

Collaborating with Dr. B. Rioja of the Aluminum Corporation of America to determine feasibility of atom-probe analysis of a newly developed class of Al-Li-Cu alloys.

Collaborating with Dr. R.D. Arollia of the General Electric Company and Prof. H. Fraser of the University of Illinois to investigate atomic structure and chemical microcomposition for a series of nickel-based superalloys.

Collaborating with Mr. J. Smith and Prof. H. Fraser of the University of Illinois on studies of three related nickel-based superalloys using field ion microscopy, transmission electron microscopy, and atom probe analysis.

Collaborating with Dr. M. J. Kaufman of the NBS Metallurgy Division on comparative studies with atom-probe field-ion microscopy and transmission electron microscopy of nickel-based superalloys and a series of Al-Li-Cu alloys.

Collaborating with Dr. J. W. Cahn of the NBS Institute for Materials Science and Engineering on investigations of the atomic structure in rapidly solidified Al-Mn alloy ribbons exhibiting icosahedral long-range order by electron diffraction.

Consulted with Dr. R. D. Young of the NBS Mechanical Production Metrology Division and Mr. S. R. Mielczarek of the NBS Radiation Physics Division on probe preparation techniques for scanning tunneling microscopy.

Powell, C. J.

Member of Solid State Physics Review Panel for Office of Naval Research.

Collaborating with Dr. M. P. Seah of the National Physical Laboratory, London on the development of plans and programs for the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards.

Stockbauer, R.

Collaborating (with R. L. Kurtz) with Drs. C. Kunz and J. Schmidt-May of the German Synchrotron Laboratory DESY, Hamburg and Dr. A. Flodström of Lund University, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. L. Kurtz) with Dr. A. Flodström of Lund University, Sweden on experiments at the NBS synchrotron radiation facility SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) angular distributions (ESDIAD) of ions desorbing from adsorbates on semiconductors.

Collaborating (with R. L. Kurtz) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. L. Kurtz and T. E. Madey) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest College on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with R. L. Kurtz) with Mr. J. Jimenez of Yale University, Prof. D. Caldwell of the University of Florida, and Dr. D. L. Ederer of the NBS Radiation Physics Division on measurements of the angular distribution of fluorescence from molecules excited by synchrotron radiation from the NBS SURF-II facility.

Collaborating with Dr. A. C. Parr of the NBS Radiation Physics Division and with Dr. D. Holland of Daresbury Laboratory, England on measurements of the fragmentation of molecules using photoelectron-photoion coincidence techniques.

Interacting with Drs. A. C. Parr, H. Hardis, and D. L. Ederer of the NBS Radiation Physics Division, Dr. J. L. Dehmer of Argonne National Laboratory, and Drs. J. B. West and D. Holland of Daresbury Laboratory, England on measurements of photoelectron angular distributions as a function of photon energy in gas-phase molecules.

Szuromi, P.

Collaborating with Drs. S. Semancik and D. F. Cox of the NBS Chemical Process Metrology Division in an investigation of the surface properties of semiconducting oxide surfaces used in gas sensing applications using ultraviolet photoemission spectroscopy. The interaction of H₂O with tin oxide (a widely used sensor material) has been studied.

Udovic, T. J.

Collaborating (with R. R. Cavanagh, R. D. Kelley, and M. J. Wax) with Dr. J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbed molecules on catalyst materials.

Collaborating (with R. R. Cavanagh) with Dr. J. J. Rush of the NBS Reactor Radiation Division and with Dr. B. J. Tatarchuk of Auburn University on neutron inelastic scattering measurements of the adsorptive behavior of hydrodesulfurization catalysts.

Wax, M. J.

Collaborated (with R. R. Cavanagh) with Dr. J. J. Rush of the NBS Reactor Radiation Division and Dr. G. D. Stucky of du Pont on the application of inelastic incoherent neutron scattering to study diffusional motion of hydrogen in zeolite rho.

Collaborated (with R. R. Cavanagh, R. D. Kelley, and T. J. Udovic) with Dr. J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbed molecules on catalyst materials.

10. VISITING SCIENTISTS

The Surface Science Division has been host during the past year to a number of scientists who have worked with the Division staff on problems of mutual interest.

Barak, D., Head of the Electronic Design Department of the Israeli Nuclear Research Center-Negev, is working at NBS for one year beginning August, 1985. He is helping to design, construct and test improvements in the angle-resolved x-ray photoelectron spectrometer (XPS) consisting of a new electron lens system and a position-sensitive electron detection system.

Benndorf, C., of the University of Hamburg, W. Germany spent two months at NBS in early autumn 1984 initiating measurements of the structure and chemistry of ammonia on both clean and alkali-promoted Fe(100).

Chambers, G. P., a graduate student at the University of Maryland, has worked at NBS this past year under a cooperative agreement. He has been involved in the development of a data base system for the compilation of evaluated sputtering yield data.

Clinton, W. L., of the Department of Physics of Georgetown University is spending five months at NBS beginning September, 1985 to perform theoretical studies relating to electron- and photon-stimulated desorption of ions and neutral species from surfaces.

Flodström, A., of Lund University, Sweden worked at NBS between May and August, 1985. He initiated a study of adsorbate structures on semiconductor surfaces using ESDIAD, participated in photon-stimulated desorption measurements from non-maximal-valent oxides, and cooperated in the set up and calibration of a new toroidal grating monochromator at SURF-II.

Hashiguchi, Y., of the Nippon Steel Corporation, Japan has worked at NBS since March, 1985 on a one-year assignment. He is studying the interface-width dependence on ion bombardment parameters as well as collisional excitation and laser ionization of sputtered atoms.

Holloway, S., of the University of Liverpool visited NBS for two weeks during the summer of 1985 to work on theoretical modeling of reactive molecular processes at surfaces.

Jansen, W. R., a graduate student of the Twente University of Enschede, The Netherlands worked at NBS for three months in the fall of 1985. He extended the existing computer software for automated XPS measurements to permit operation in a timesharing mode, completed the interfacing of the computer to the XPS sweep supply, and extended the data reduction software.

Jimenez, J., a graduate student of Yale University, used the surface science beam line at SURF-II for three months during the fall of 1985 to study the angular distributions of fluorescence from gas-phase molecules.

Karikorpi, M., a graduate student of the University of Liverpool visited NBS for two weeks during the summer of 1985 to work on theoretical modeling of reactive molecular processes at surfaces.

Roovers, A. D., a graduate student of the Twente University of Technology, Enschede, The Netherlands, worked at NBS for three months in the fall of 1984. He wrote the basis system software to automate the angle-resolved XPS instrument with a minicomputer as well as basic software for data reduction.

Shinn, N. D., of Sandia National Laboratory, Albuquerque, NM, is spending four months at NBS during the fall of 1985 studying adsorbed molecules on metal surfaces using high-resolution electron energy-loss spectroscopy.

Tanuma, S., of the Nippon Mining Company is working at NBS on a two-year assignment beginning August, 1985. He will be participating in measurements of core-level binding energies by different electron-spectroscopic methods and in calculations of electron inelastic mean free paths in solids.

CHEMICAL KINETICS DIVISION

S. E. Stein, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

1. INTRODUCTION

A. Background

The objective of chemical kinetics is to understand the critical factors controlling chemical change and reactivity. It seeks to both interpret chemical change in terms of individual molecular events and develop quantitative theoretical models for these events. The societal importance and exciting scientific opportunities in this area are well documented in the Pimentel Report to the National Academy of Sciences on "Opportunities in Chemistry" (National Academy Press, Washington, D.C., 1985). In this report chemical kinetics is listed as the first of seven "Intellectual Frontiers in Chemistry" where the greatest opportunities for major advances lie. Understanding Chemical Reactivity is given as the first of five priority areas where continued growth can "provide the basis for U.S. competitive advantage in development of new processes, new substances, and new materials". Moreover, chemical kinetics is an important component of each of the other four priority areas, especially in the Chemistry Around Us and Chemical Behavior Under Extreme Conditions areas.

The breadth and vitality of this area were also evident in the first International Conference on Chemical Kinetics, held at NBS this summer. Over 100 poster presentations and 30 invited talks spanned a wide range of chemical reaction systems and experimental methods. A sampling of areas represented were a priori calculations of potential energy surfaces, rate measurements of organic and organometallic species in solution, state-to-state energy transfer determinations and ion-molecule rate measurements. Underlying this striking diversity was a common concern for transition states and for the basic molecular properties determining reactivity. The proceedings of the conference will be published in the Journal of Physical Chemistry (see Section 2.B for additional details).

Exciting experimental breakthroughs and theoretical developments have been made over the last few years that have dramatically expanded the breadth and depth of the discipline. Experimentally, largely as a result of advances in laser and computer technology, a new array of instrumentation has been developed with improved precision and sensitivity which is now yielding increasingly varied and detailed kinetic information. Spurred on by practical concerns such as combustion, these new instruments,

alongside more established techniques, have brought certain areas of kinetics to a high degree of development where practitioners are on the verge of devising reliable theories with broad predictive power. The development of these theoretical tools is of critical importance to the field, since they provide frameworks for interpreting as well as generalizing results of individual experiments.

While the number and diversity of reactions investigated by kineticists are increasing at a rapid pace, the area has actually become more cohesive as interrelations between formerly divergent areas become increasingly clear. For instance, unimolecular reaction rate theories developed for neutral species are being widely used to explain critical features of gas-phase ion-molecule chemistry. In a similar manner, results of gas-phase ion chemistry are beginning to provide a solid conceptual foundation for solution ion chemistry, a poorly understood area of immense practical importance.

B. Scope

Over the past several years the scope of research within the Chemical Kinetics Division has expanded significantly. Just four years ago its primary emphasis was on gas-phase reactions of neutral species. Through recent additions of staff and changes in research direction, it is now roughly equally divided into groups studying ion and neutral reactions and on studies in the gas and condensed phases. In addition, the data centers (ion and neutral) are broadening their efforts in kinetic data evaluation.

Since predictive theories are required by both experimentalists and "data evaluators", advancement of these theories provides a key unifying factor for the diverse activities in the division. In fact, it is expected that the Division will ultimately be able to offer not only NBS evaluated data but also NBS "calibrated" predictive models for data not currently available.

Central to the broadening of the Division's scope have been two competency development programs. One, entitled "Transformations of Complex Organic Compounds", has enabled us to add personnel and equipment in order to apply the exact principles of small molecule kinetics to reactions of more complex substances. The second program, "Kinetic Studies of the Effects of Ionizing Radiation" has enabled the growth of existing programs on gas-phase ion-molecule chemistry to include more complex reactions in both the gas phase and solution.

C. Activities

Most activities within the Chemical Kinetics Division fall within one of two distinct, but closely interacting areas, kinetic measurement and data evaluation. In the former area we both develop new measurement techniques and determine rates and mechanisms of selected chemical processes. These new techniques either allow monitoring reaction intermediates not observable by existing techniques (two new techniques

are multiphoton ionization and modular MS/MS spectrometry) or enable kinetic measurements to be made in unique, hard-to-study chemical environments (examples are studies of large species at high temperatures using heated shock tube, flow ESR and novel laser heating techniques). We measure rates, determine products and develop reaction mechanisms for selected simple processes needed for the interpretation of complex, practical processes. Special attention is given to those cases where a small number of measurements can yield a broad advance in predictive theory. A wide range of programs of this nature are underway including reactions of ions and neutral molecules in both the gas and condensed phases.

Other programs are devoted to the theoretical analysis of important reacting systems too difficult to fully analyze by experimental means. An example is our development of a chemical theory of graphite and very large polyaromatic molecules.

Data center activities and associated theoretical studies are at the heart of the division's activities. This work not only organizes a wide spectrum of kinetic data and thermodynamic properties of reactive intermediates, but also utilizes this data to extract general reactivity patterns and develop improved predictive theories. Major areas of uncertainty revealed in the course of evaluation activities often prompt studies in one of our experimental programs. Moreover, the considerable breadth of ongoing experimental activities in the division ensures that insight needed for thorough data evaluation is available.

Over the past year we have made considerable progress in upgrading our instrumentation. Construction of a substantial portion of a laboratory for detection of transient species by multiphoton ionization (MPI) is complete. A high resolution "reflection" mass spectrometer is under construction which will significantly improve the resolution and sensitivity of these MPI experiments. A custom-designed, modular triple quadruple mass spectrometer is now operational after some initial installation problems. We are in the process of adding an excimer photolysis source and multichannel vacuum UV detection for our flash photolysis experiments.

This has been an exceptionally productive year. Both the total number of research publications (58 published, 55 in press or submitted) and the number per research staff member (3.9, 3.7) are at an all-time high for our division. Viewed in another way, the net cost per published paper was \$44,000, comparable to that for productive academic institutions and well below that for research institutes. Moreover, the cost per publication in terms of NBS base support was only \$21,000. A major reason for this increased productivity was the very large number of guest workers attracted to our division (21 individuals, see Section 10). Another reason was the maturation of our two competence-development initiatives.

D. Services to Other Bureau Programs and Other Agencies

The Chemical Kinetics Division serves as a technical resource for a wide range of external programs. This activity is an integral part of our mission, and a key means of applying our scientific expertise to industrial, defense, and environmental problems. Moreover, these projects are directly related to, and strongly supportive of, the basic long-range scientific objectives of the division. In FY 85 we participated in the following NBS and other agency programs:

Office of Standard Reference Data

- The Chemical Kinetic Data Centers (ion and neutral) for data compilation and evaluation.

Department of Energy

- Compilation and evaluation of combustion chemistry data
- Chemistry of hazardous waste incineration
- Pulse radiolysis studies of electron transfer in solution
- High pressure mass spectrometric studies of ion kinetics and thermodynamics.

Department of Defense

- Chemical theory of carbon
- Kinetics of the decomposition of nitroaromatics
- Multiphoton ionization processes
- Tandem mass spectrometric studies
- Ion-cyclotron resonance studies of ion-molecule condensation processes in hydrocarbons.

National Aeronautics and Space Administration

- Elementary kinetic studies of stratospheric reactions
- Chemical kinetics of planetary atmospheres
- Evaluation of stratospheric chemical kinetic data

Environmental Protection Agency

- Acid rain chemistry

2. DATA CENTERS

R. J. Cvetanovic, J. T. Herron, R. F. Hampson, Jr., R. D. Levin,
S. G. Lias, W. Tsang, F. Westley and G. W. Zumwalt

A. Introduction

The Chemical Kinetics Division contains two closely related but distinct data centers, the Chemical Kinetics Data Center (headed by J. T. Herron) and the Ion Kinetics and Energetics Data Center (led by S. G. Lias). They are responsible for providing compilations and evaluations of numerical data on the kinetics of chemical reactions, and the thermochemical properties of ionic and free radical species. They provide this information to chemical kineticists and to scientists in other disciplines, such as the analytical and biological sciences, and to modelers of very complex chemical systems such as encountered in combustion and atmospheric chemistry. Although the major sources of information contained in the existing data bases are experimental studies, a major goal is the development and application of theoretical methods for both the analysis and extrapolation of existing experimental data, and the prediction of the behavior of chemical systems for which there is no data. Over the past year the Data Centers have pooled resources in the areas of archival article acquisition, development of publication procedures, and design and implementation of a Data Base Management System.

B. Chemical Kinetics Data Center

(J. T. Herron, R. F. Hampson, Jr., W. Tsang, F. Westley
G. W. Zumwalt and R. J. Cvetanovic)

There are four primary goals of the Chemical Kinetics Data Center. (1) To provide compilations, bibliographies and evaluated chemical kinetics data bases for neutral species in support of science and technology. (2) To develop new or improved theoretical models for the prediction of chemical kinetic data. (3) To develop cost effective methods for the acquisition and evaluation of chemical kinetic data. (4) To disseminate chemical kinetic data to the scientific and technical community. This center has served for many years as a national resource in supplying evaluated chemical kinetic data, data compilations, and annotated bibliographies covering a broad range of scientifically and technologically important systems. We have been involved in the chemistry of stratospheric ozone depletion since it was first recognized as a serious problem, and continue to assist in providing the authoritative chemical kinetic data base used in modeling stratospheric chemistry. We provide data compilations and evaluations which address critical problems in combustion chemistry and allow a more thorough testing of kinetic theory.

One of our major goals in the area of data evaluation is to provide a definitive set of evaluated rate data for use in combustion modeling. This activity is supported by the Office of Basic Energy Sciences of DoE. The first major output of that program, "Chemical Kinetic Data Base for Methane Combustion", is complete and has been accepted by the Journal of Physical and Chemical Reference Data for publication. It is available on a limited basis as an NBS Internal Report (NBSIR 84-2913). It provides explicit expressions at 0.1, 1, and 10 atmospheres for the rate constants for reactions in the fall-off region. It contains data on 235 reactions with a total of 293 separate entries. This evaluation relies heavily on the application of transition state and unimolecular reaction rate theory to fit data measured over a wide range of temperature and pressure. The theoretical framework indicates that much of the data given in the older literature is valid and that it is possible to derive rate expressions for many reactions over the entire range of temperature and pressure encountered in a practical combustion systems.

This work has been extended to include reactions of CH_3OH , CH_2OH , C_3H_8 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $t\text{-C}_4\text{H}_9$, and $i\text{-C}_4\text{H}_{10}$ with species in the methane data base, among themselves, and in unimolecular reactions. This encompasses a total of 164 new reactions. The evaluated data base now includes 399 reactions which corresponds to about 550 separate elementary reactions when all reaction channels are accounted for.

In addition to kinetic data, this evaluation provides, whenever possible, the thermal functions for each species. These are either taken from existing sources (e.g. JANAF Tables) or are independently derived.

In the coming year the data base will be expanded to include reactions of atomic oxygen with organic compounds. The number of reactions involved is several hundred. The total data base will then consist of over 750 evaluated chemical reactions.

A related project on developing a compilation of experimentally determined rate constants for combustion reactions continues. Papers for the period 1977-1982 have been abstracted and all data entered into our HP-1000 computer system. A manuscript version of this compilation is under preparation and will be submitted for publication in early 1986. Work has also been finished on abstracting data published in 1983. For 1984, relevant articles have been identified and acquired, and abstracting initiated. This bibliographic activity is the prelude for the critical evaluation of combustion data for systems more complex than methane. In the coming year we expect to have identified and abstracted data from all articles published through 1985.

An evaluation of stratospheric reactions of halogen-containing species was completed as part of the Data Center contribution to the NASA Panel for Data Evaluation and has been published by the Jet Propulsion Laboratory. These data were also reviewed and evaluated for the CODATA Task Group on Chemical Kinetics. The complete report of that task group

has now been published in the Journal of Physical and Chemical Reference Data. This will be the final publication in this series following the discontinuation by CODATA of this activity. The part of this activity supported by NASA will continue in the coming year.

A new activity in the area of the chemistry of dielectric breakdown of SF₆ and the broader area of plasma chemistry was initiated this year. Before the chemical kinetics could be treated, it was necessary to assemble and evaluate a thermochemical data base for the species of interest. A manuscript, containing thermochemical data on 38 substances containing S, F, O, and H has been prepared. Table 1 is a summary of the recommended values provided in that work. Chemical kinetic data for the reactions of SF₄, SF₅, and S₂F₁₀ have been reviewed and recommended rate parameters provided for the relevant elementary reactions based on computer modeling fits of experimental data. This work is included in a manuscript under preparation.

The plasma chemistry program will continue through joint activities with the Electrosystems Division and JILA on modeling aspects of SF₆ breakdown and relaxation. Particular attention will be paid to secondary reactions involving O₂, H₂O and O.

The development of a data base management system continues under the direction of R. J. Cvetanovic. Most work on the identification and nomenclature of inorganic and organic compounds is complete. Work on the actual searching routines for chemical reactions is underway and should be largely complete this coming year. Each component of the system is being tested on a suitably designed data base.

A major objective in the coming year will be the completion of this database management system and the conversion of existing data bases into forms suitable for inclusion in the new system. Progress in developing software for the new system has reached the point at which search routines for chemical reactions are being tested and modifications made based on an analysis of the test runs. We will continue to work closely in this endeavor with the Ion Energetics and the Chemical Thermodynamics Data Centers. We will also be considering various options concerning the identification, abstraction, and entry of data into the new system.

The Chemical Kinetics Data Center will expand it's scope to cover a broader range of gas phase reactions of neutral species. The Director of the Data Center will become responsible for the identification of articles to be abstracted from the primary archival literature starting with papers published since December 31, 1984. Papers related to any aspect of the reactions of neutral species in the gas phase will be abstracted. This will include theoretical articles and condensed phase data which are applicable to the gas phase. The major thrusts of the data center in the coming year will remain that of completing the database management system, and continuing the evaluation and compilation activity in combustion chemistry.

Table 1. ΔH_{f298}° and S_{298}° for some S-F-O Molecules, Radicals, and Related Compounds^a

Species	ΔH_{f298}° , kcal	S_{298}° , cal	Source
F	18.86±0.40	37.917	[5]
S	66.20±0.06	40.086±0.008	[2]
SF	3.1±1.5	53.8±0.2	[3]
SF ₂	-70.9±4.0	61.57±0.02	[3]
SF ₃	-116.7±0.5	68.4±1.0	ΔH_f calculated from [6], S from [2]
SF ₄	-182.4±5	71.6±0.1	[3]
SF ₅	-218.1±3.2	72.8±2.0	ΔH_f calculated from [6], S from [2]
SF ₆	-291.7±0.2	69.7±0.1	[3]
S ₂	30.71±0.07	54.506±0.012	[2]
SSF	(-2±7)		
SSF ₂	-71±5	69.96±1.0	ΔH_f calculated from [3], S from [3]
FSSF	-68±5	70.26±0.02	ΔH_f calculated from [3], S from [3]
SFSF ₃	-158±6	79.8±1.2	ΔH_f calculated from [11], S from [11]
S ₂ F ₆	(-270±15)		
S ₂ F ₈	(-375±15)		
S ₂ F ₉	(-408±8)		
S ₂ F ₁₀	-482±6	94.9±2.0	ΔH_f from [21], S from [2]
O	59.554±0.024	38.468±0.005	[2]
FO	26±10	51.77±0.3	[5]
FO ₂	3.0±5	61.9	[5]
F ₂ O	5.86±0.38	59.12±0.1	[5]
OS	1.2±.3	53.020±0.01	[2]
•OSF	(-45±7)	(62±2)	
OSF ₂	(-113±8)	66.69±0.1	S from [4]
•OSF ₃	(-149±10)	(72±2)	
•OSF ₃	(-136±8)	(72±2)	
OSF ₄	(-223±11)	74.726	S from [17]
•OSF ₅	(-237±4)	(70±2)	
O ₂ SF ₂	-181.3±2	67.76±0.1	[4]
O ₂ SF ₅	(-232±4)		
H	52.103±0.001	27.392±0.004	[2]
HF	-65.14±0.2	41.508	[5]
SF ₃ (OH)	(-189±8)		
SF ₄ (OH)	(-216±5)		

^aAll values in parentheses are estimated

A highlight of the past year was the holding of the International Conference on Chemical Kinetics at NBS on June 17-19. This meeting, organized by the Director of the Data Center, was designed to bring together a cross section of leading kineticists involved in theoretical and experimental aspects of gas and condensed phase chemistry of neutral and ionic species. The meeting was attended by 192 scientists from the United States, Europe, Canada, South America, Asia and Australia. Funding for the meeting was obtained from AFOSR, EPA, GRI, NASA, NSF and NBS. The meeting was highly successful as indicated by the quality of invited and contributed presentations and the vigor of the discussion periods. It also illustrated in a very convincing fashion the inseparability of theory and experiment which has a direct bearing on the evaluation of chemical kinetic data. A selection of papers from the meeting will be published in a special issue of the Journal of Physical Chemistry.

C. Ion Kinetics and Energetics Data Center
(S. G. Lias and R. D. Levin)

The goals of the Data Center are to collect and maintain an up-to-date file of experimental data pertaining to the thermochemistry of ions (ionization potentials, appearance potentials, and equilibrium constants) and the kinetics of ion-molecule reactions, to make compilations of these data and to publish evaluations of the collected data for use by the scientific and technological communities.

The Data Center is closely associated with the Ion Kinetics Group which, as described in Section 4., can supply benchmark measurements of ion thermochemical quantities to aid in data evaluation activities.

(1) Publications during past year:

"Evaluated Gas Phase Basicities and Proton Affinities of Molecules; Heats of Formation of Protonated Molecules" Sharon G. Lias, Joel F. Liebman, and Rhoda D. Levin, Journal of Physical and Chemical Reference Data 13, 695-808 (1984).

This comprehensive review of the field of gas phase proton affinity measurements included evaluated gas basicities and proton affinities for 784 atomic and molecular species, and an annotated bibliography of references on gas phase proton affinity determinations. To date, more than 150 reprints have been sent to requesting laboratories worldwide. An up-date, including references to 28 relevant papers which appeared since the compilation went to press, was prepared and distributed with the requested reprints.

"Absolute Values of Gas Phase Proton Affinities and Basicities of Molecules: A Comparison Between Theory and Experiment," D. A. Dixon and S. G. Lias, Molecular Structure and Energetics (J. F. Liebman and A. Greenberg, editors) Verlag: Florida (in press).

This invited book chapter grew out of collaborative contacts between the Data Center and Dr. David A. Dixon of the E. I. DuPont de Nemours Company. Dr. Dixon carried out a comprehensive evaluation of theoretical determinations of proton affinities as a result of discussions with Data Center personnel during the preparation of the compilation on the same subject. This publication is a preliminary presentation of a larger work on the evaluation of theoretical proton affinity data.

(2) In preparation:

"Ion Thermochemistry" by S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, and R. D. Levin.

This comprehensive and complete compilation of evaluated heats of formation of more than 3000 positive and negative ions, to be submitted for publication in the Journal of Physical and Chemical Reference Data, is currently being up-dated to include data which have appeared in the literature since our earlier publication of data archives covering the years 1971-1981 (R. D. Levin and S. G. Lias, "Ionization Potential and Appearance Potential Measurements, 1971-1981"). As a result of this effort, the publication will be nearly up-to-date at the time of publication. Most of the recent data have been abstracted; current work involves entering the new data into the computer and obtaining the auxiliary thermochemical information and drawings needed for the publication. The data for the years before 1981 have been evaluated, entered into the computer data base designed for the project, and computer printouts of that material have already been exhaustively checked and proof-read.

The list of authors of this forthcoming publication includes several outside collaborators, who bring specialized expertise to the project. Dr. J. E. Bartmess of the University of Tennessee is an expert on the thermochemistry of anions, a field in which he has published extensively. Dr. J. L. Holmes of the University of Ottawa is one of the foremost leaders in measurements of appearance potentials of ions, and derivation of thermochemical and structural information on ions from mass spectrometric data; his collaboration on the project was sought after it was learned that he had collected and evaluated a vast archive of data on organic ions containing oxygen and nitrogen for the use of himself and his students. Dr. Joel F. Liebman of University of Maryland, Baltimore County is a theoretical organic chemist specializing in bonding theory and the estimation of thermochemical data; as an integral part of this project, he has collected a vast archive of heats of formation of organic and inorganic compounds from the experimental literature, and has estimated more than a thousand additional heats of formation.

3. KINETICS OF NEUTRAL SPECIES

R. Billmers, W. Braun, R. L. Brown, A. Fahr, L. L. Griffith,
J. W. Hudgens, M. J. Kurylo, A. Laufer, M. Manka, G. Z. Mallard,
R. I. Martínez, P. Ouellette, D. Robaugh, M. D. Scheer, S. E. Stein,
W. Tsang, and J. A. Walker

A. Introduction

This program is concerned with the mechanisms and rates of chemical transformations at the elementary single step level. We determine reaction mechanisms, measure rate constants, develop measurement methods and test theoretical formulations. The activities of the group span all three phases and include processes involving single atoms as well as large organic moieties. The concentration on elementary processes leads to a special focus on free radical reactions. Accordingly, we develop methods for the detection of free radicals and we are concerned with the processes that lead to their generation and destruction. We also study their reactions with each other, as well as with stable substrates. A considerable amount of the group's activities is concentrated on the kinetics of reactants in thermal equilibrium. At the same time our activities include the study of unimolecular kinetics in the fall-off region and intermolecular energy transfer involving large polyatomic species. In order to extend the range of our measurements, we are particularly interested in the development and testing of predictive theory.

The programmatic aim of the group's activities is the understanding of chemical change at the elementary single step level. This "understanding" is made more meaningful by the possibility of using such data as inputs for computer simulation and all the attendant possibilities of its use as a substitute for expensive and uncertain physical testing. With the revolutionary advances in computer technology, there is little question that this line of research will continue to grow. Programs in this group are designed to assure the proper exploitation of this emerging technology by making available the best available input data. Currently, we are focusing on the areas of stratospheric and high temperature chemistry. Members of this group interact closely with internal and external efforts aimed at developing the best possible data base for such efforts. Indeed, much of the data evaluation effort has been carried out by group members.

The large amount of other agency support obtained by members of this group, together with other signs of scientific vigor such as a substantially larger number of publications per person, makes it clear that the group has had a very successful year. Finally, we would like to call attention to the retirement of two of the senior members of this group; James A. Walker, after 41 years service and Milton D. Scheer with 31 years of service. We are fortunate in being able to retain their services as contractors and thereby continue to benefit from their many years of experience.

In the following sections we describe in detail the activities of the group during the past year. They are divided into studies in the gas phase (B) and the condensed phase (C).

B. Gas Phase Kinetics.

(A. Fahr, M. J. Kurylo, A. Laufer, G. Mallard, R. I. Martinez, P. Ouellette, D. Robaugh, S.E. Stein, W. Tsang, J.A. Walker)

1. Stability and Reactivity of Large Polyatomic Species

This activity is a central part of our competence program, "Transformation of Complex Organics." It seeks to develop a detailed understanding of the stability and reactivity of large polyatomic molecules. As a result, the emphasis of the work is on the understanding of mechanisms and the measurement of thermal rate constants. We are particularly concerned with aromatic systems. The stability of such systems make them the inevitable end products in hydrocarbon transformations under high energy conditions. As such they are of major concern in technological problems such as soot formation and hazardous waste disposal. Much of the current work is concerned with pyrolytic reactions. In the future we will be increasingly concerned with oxidative processes.

(a) Very Low Pressure Pyrolysis Experiments: Phenyl Radical Reactions With Ethene and Acetylene at High Temperatures

(G. Mallard, A. Fahr and S. E. Stein)

Phenyl radicals are thought to be important intermediates in high temperature reactions leading to polycyclic aromatic hydrocarbons. These radicals and related species have been postulated as intermediates in benzene polymerization mechanisms and appear to play a role in thermal reactions of polycyclic aromatic hydrocarbons. They are also likely to be central in the mechanism for soot production in rich flames. While a large body of data exists for liquid phase reactions, most is at room temperature, and the specific reactions of importance in high temperature systems have not been studied.

The important reactions, from the point of view of the build up of polycyclic aromatic hydrocarbons from simple fuel molecules, are the addition of phenyl radicals to unsaturated bonds. The pyrolysis of any alkane leads to large quantities of ethene and acetylene at high temperatures. The reaction of phenyl radicals with these species is thus likely to dominate the chemistry of molecular build-up beyond the phenyl radical. The addition to ethene and acetylene, two major species in pyrolytic reactions, to produce styrene and phenylacetylene are expected to be critical steps. Rate constants for these steps were measured using the techniques of very low pressure pyrolysis adapted to the study of bimolecular reactions.

The rate constants for H-atom displacement resulting from phenyl radical addition to ethene and acetylene were measured relative to the rate constant for phenyl radical recombination. The ratios found were:

$$k_{\text{add}}/(k_{\text{rec}})^{1/2} = 103.46 \pm 0.55 \text{ (M}^{-1}\text{s}^{-1}\text{)}^{1/2} \text{ at 1066K for C}_2\text{H}_2 \text{ and} \\ 103.44 \pm 0.18 \text{ (M}^{-1}\text{s}^{-1}\text{)}^{1/2} \text{ at 1028K for C}_2\text{H}_4 \text{ .}$$

Assuming that the recombination rate constant for phenyl radicals is the same as that for a number of large hydrocarbon radicals ($10^{9.5} \text{ M}^{-1}\text{s}^{-1}$), the addition rate constants are found to be

$$k_{\text{add}} = 10^{8.21 \pm 0.55} \text{ M}^{-1}\text{s}^{-1} \text{ for C}_2\text{H}_2 \text{ at 1066K} \\ 10^{8.09 \pm 0.18} \text{ M}^{-1}\text{s}^{-1} \text{ for C}_2\text{H}_4 \text{ at 1028K.}$$

This work was partly supported by NASA.

We are now in the process of studying reactions of phenyl radicals with benzene and diacetylene, two processes that can directly generate polyaromatic species.

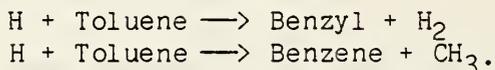
- (b) Single Pulse Shock Tube Studies: Stability of Nitroaromatics and the Hydrogen Atom Induced Decomposition of Toluene and Phenol
(W. Tsang and D. Robaugh)

Our heated single pulse shock tube has been used in studies of the thermal and chemical stability of aromatic compounds. The compounds of interest are the nitro-aromatics in the first area (with the support of the Army Research Office) and the hydrogen-atom-induced decomposition of toluene and phenol in the latter. We have made a number of interesting new observations and laid the basis (supported by DoE) for future research.

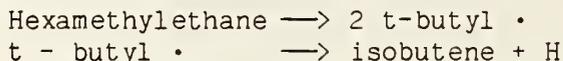
In last year's report we described our initial experiments with nitrobenzene decomposition. The experimental results are consistent with a dual thermal decomposition mode; C-N bond cleavage and isomerization to form the nitrite prior to N-O bond cleavage. The prime mode for decomposition of ortho-nitrotoluene, studied this year, is clearly not through these two processes. On the other hand para-nitrotoluene behaved like nitrobenzene. Our evidence for this conclusion is the failure in the decomposition of the ortho compound to recover more than 40% of the expected yields of toluene and ortho cresol, while for nitrobenzene and para-nitrotoluene mass balance was obtained. Considerable effort was devoted to deducing the nature of this new process with as yet very little success. There are a number of processes which we know do not occur; for example, HONO elimination or isomerization and decomposition to form the alcohol. We are coming to the conclusion that this new pathway does not involve removal of the nitrogen from the ring. Currently, we are carrying out experiments to check this hypothesis. It is interesting that in the earlier studies of Fields and Myerson using a flow system, [J. Org. Chem., 33, 4487, 1968] ortho-nitrotoluene also displayed pathological

behavior since it was much less stable than other nitroaromatics and its decomposition led to large yields of aniline. They attributed this to a surface process. Since surface reactions cannot occur in a shock tube, it appears that there is a complex molecular rearrangement occurring in ortho nitrotoluene decomposition. In the course of carrying out this work we have also determined the rate of C-NO₂ bond cleavage for the two nitrotoluene compounds. For the three nitroaromatic compounds the relative rates are 3:1.5:1 for ortho-nitrotoluene:nitrobenzene:para-nitrotoluene, respectively. The effect of methyl substitution is, as expected, rather small. This is in contrast to similar experiments at SRI using laser heating via energy transfer through SF₆, where ratios of the order of 60:10:1 were obtained. This may be due to the extreme inhomogeneity, both in space and time, of the laser experiments.

Until this year, all our single pulse shock tube work has concentrated on unimolecular reactions. We have now taken the first steps toward extending this methodology towards the study of high temperature bimolecular processes. The first reactions that have been studied are:



These are important reactions in high temperature aromatic chemistry and accurate determination is made difficult by the two reaction channels. Our approach has been to use hexamethylethane as the hydrogen atom source through the reactions,



In sufficiently large excesses of toluene (>100 to 1) every isobutene formed releases a hydrogen atom into the system. The ratio of (isobutene-benzene)/benzene is a direct measure of the relative rate constant for abstraction and displacement. If we now add into the system large quantities of methane, the decrease in benzene yield is directly relateable to the hydrogen abstraction from methane. Since the rate constant for this process is well established we can then place these results on an absolute basis. The rate expressions at 950-1100K for the two processes are,

$$\begin{aligned} k(\text{displacement}) &= 9.0 \times 10^9 \exp(-2240/T) \text{ M}^{-1} \text{ s}^{-1} \\ k(\text{abstraction}) &= 1.1 \times 10^{11} \exp(-3900/T) \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

The abstraction must be exclusively from the benzylic position (the maximum rate for hydrogen abstraction from the benzene ring is estimated to be a factor of 30 slower). The activation energy for abstraction demonstrates that only half of the benzyl resonance energy contributes toward lowering the reaction barrier. For the displacement reaction the results indicate that hydrogen addition is little affected by methyl substitution. A paper on this work has been completed and will be submitted to the Journal of Physical Chemistry.

With the partial support of the Department of Energy, are now using this method to study hydrogen atom attack on phenol. Equally exciting is the prospect of obtaining an entire series of high accuracy relative rate constants between various pairs of reactants. Thus, as we determined the rate constants for hydrogen attack on toluene from studies in the presence of methane, then the addition of ethane in the presence of traces of hexamethylethane in toluene will permit us to determine the rate constant of hydrogen attack on ethane from ethylene yields as referenced against the rate for attack on toluene. We believe that we can measure these relative rates with an accuracy of a few percent. It should therefore be possible to make drastic improvements in the accuracy of kinetic data obtained at high temperatures.

(c) Data Evaluation: Stability of the Cyclohexadienyl Radical
(W. Tsang)

Our interest in the reactions of hydrogen atoms with unsaturated organics have led to an investigation of the stability of cyclohexadienyl radicals. Nicovich and Ravishankara (J. Phys. Chem., 88, 2534, 1984) have recently reported the rate expression

$$k(\text{C}_6\text{H}_7 \rightarrow \text{C}_6\text{H}_6 + \text{H}) = 1.5 \times 10^{16} \exp(-32000/RT)/\text{s}$$

This large A-factor is characteristic of bond breaking reactions to form two radicals and is different from what has been derived for alkyl radicals decomposing to alkene + H. We have reanalyzed the experimental data on the basis of a third law approach (i.e., using an estimated value for the entropy of the cyclohexadienyl radical). We first demonstrate that the high A-factor in combination with the well established rate expression for the reverse process implies an intrinsic entropy for cyclohexadienyl radical that is much smaller than that for benzene. This is an unlikely possibility. Assumption of a more reasonable frequency assignment for cyclohexadienyl using as a basis the assignments for benzene, 1,4 cyclohexadiene and cyclohexene leads to a new value for the entropy of cyclohexadienyl. When this is combined with the measured equilibrium constant (from $k_f/k_r = K_{eq}$) at the midpoint of the experimental determinations, a new heat of formation for cyclohexadienyl is calculated. Combination of the new thermochemistry with the rate expression for the reverse addition process leads to

$$k(\text{C}_6\text{H}_7 \rightarrow \text{C}_6\text{H}_6 + \text{H}) = 1.5 \times 10^{13} \exp(-28000/RT)/\text{s}$$

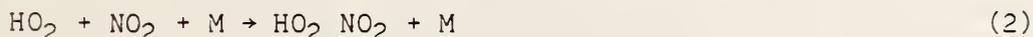
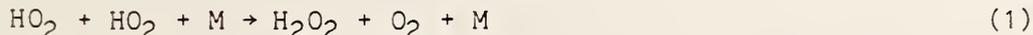
The A-factor on a per hydrogen atom basis is, within experimental uncertainty, the same as that which we calculated previously for the decomposition of alkyl radicals, even though the structure of the molecules are rather different. It demonstrates the localized nature of the structure of the transition state and the applicability of group-additivity. In the coming year we intend to apply the same procedures for analysis of OH radical attack on unsaturated compounds.

unsaturated carbene; experimental data on its properties should provide crucial tests of theory and improve our understanding of more complex carbenes.

(a) Reactions Involving Hydroperoxy Radicals
(M. J. Kurylo and P. Ouellete)

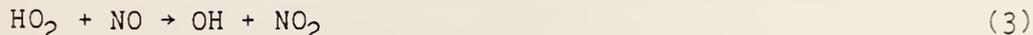
This program employs spectroscopic techniques for the detection and chemical characterization of small gas-phase free radicals. The reactive behavior of these species has many applications, for example, stratospheric ozone depletion, hazardous waste incineration, combustion, and planetary atmospheres.

During the past year, we have focused attention on the measurement of the rates of reactions involving the hydroperoxy free radical (HO_2). This species is an important chemical intermediate in both combustion and atmospheric chemistry and its reactions are characterized by complex pressure effects. With the partial support of the NASA Upper Atmospheric Research Program, we have used flash photolysis, kinetic absorption spectroscopy to study the reactions



with $\text{M} = \text{O}_2$ and N_2 . Our results for reaction (1) support the body of recent laboratory data which indicates the existence of both a bimolecular and pressure dependent component for k_1 . A statistical analysis of the combined $\text{N}_2 + \text{O}_2$ data base permits calculation of a rate constant expression suitable for use in atmospheric modeling. Our experience in the mathematical analysis of second order decay curves gained in this investigation indicates a high potential for systematic error in such fitting. A manuscript giving full details about the experiments and the data reduction has been accepted for publication in the Journal of Physical Chemistry.

Experimental conditions suitable for the measurement of k_2 are far more restrictive than those employed in the study of reaction (1). For example, contributions to the HO_2 loss by reaction (1) must be minimized and any residual effects accounted for. Corrections, however, can be made utilizing a knowledge of the initial concentration of hydroperoxy radical. Other interferences due to reaction (3)



can be minimized by restricting the amount of NO formed via NO_2 photolysis through use of appropriate flash lamp filtering. The pressure dependencies observed for both N_2 and O_2 can be described by fitting the data to the formula recommended by Troe and coworkers,

$$k(\text{M}) = \{k_{\text{O},\text{M}}[\text{M}] / (1 + k_{\text{O},\text{M}}[\text{M}] / k_{\infty})\} 0.6^{1/\alpha}$$

where $\alpha = 1 + \{\log(k_{o,M}[M]/k_{\infty})\}$. Using this analysis there appears to be a slight systematic difference between our results and those of another recent laboratory investigation. While this difference at 298K is certainly within the quoted uncertainty limits of both studies, future experiments should shed more light on its significance. A second manuscript scheduled to appear in the Journal of Chemical Physics presents a more detailed discussion of these experiments.

During the forthcoming year, we plan to extend our investigation of reaction (2) to lower temperature thereby gaining information regarding the temperature dependence of k_2 in the fall-off region. Such information allows one to calculate much needed thermodynamic parameters for peroxyntic acid (HO_2NO_2). In addition, information on the temperature dependence of k_2 , particularly in the low pressure region of the fall-off curve, is of critical importance in assessing the role of this reaction in stratospheric chemistry.

We intend to continue our investigation of the kinetics of small oxygen-containing free radicals by initiating measurements on the cross-disproportionation reaction between HO_2 and CH_3O_2 . During our early work on the HO_2 self-reaction we were able to calculate, via computer modeling, the optimal experimental conditions for this investigation. This reaction is important both in the atmospheric oxidation of methane and other hydrocarbons and in low temperature combustion systems. From a theoretical standpoint, such results should lend themselves to thorough analysis in view of the rather good data bases existing for the relevant self-reactions, $\text{HO}_2 + \text{HO}_2$ and $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$. Experiments are planned in which both the HO_2 and $^3\text{O}_2$ will be monitored by absorption spectroscopy. However due to the large differences in the self reaction rates of the two radicals, such dual measurement will not be possible for all sets of initial concentrations.

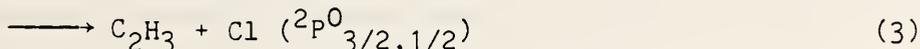
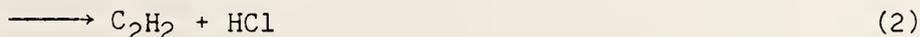
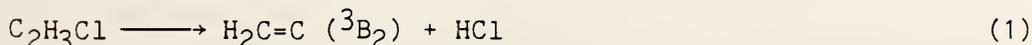
During the past year, we have collaborated with members of the Center for Analytical Chemistry in designing and fabricating an apparatus for HO_2 detection by infrared diode laser spectroscopy (including second harmonic detection). To date, an apparatus has been partially constructed and most of the needed equipment procured. The diode laser spectrometer is expected to be available for our extended use this fall. In addition to focussing on the sensitivity of the infrared detection, we intend to make measurements on pressure broadening coefficients and the effect of water solvation on the measured line strengths. Hopefully, this collaboration will pave the way for future joint projects.

(b) Reactions of Biradicals and Unsaturated Free Radicals
(A. Fahr and A. Laufer)

The objectives of this program are to produce and chemically characterize biradicals and unsaturated free radicals through flash photolysis using vacuum ultraviolet kinetic spectroscopy to follow species concentrations. Gas chromatography is used for end-product analysis. Isotopic substitution is used to clarify mechanistic processes.

Our recent efforts, supported by the NASA Planetary Atmospheres Program, are directed towards understanding the mechanism of formation and the chemistry of the vinylidene unsaturated biradical (H_2CC). This species, the smallest of a large class of unsaturated biradicals, was initially identified by us on the basis of its characteristic absorption in the vacuum ultraviolet. We have determined that the particular state of vinylidene under observation is the lowest lying excited triplet, about 1.7 eV (40kcal/mol) above the ground singlet state. The particular excited state is metastable with respect to the ground singlet state as there is a 45 kcal/mol barrier to its isomerization to acetylene. The intermediate is quite stable requiring about 10^4 collisions to quench.

We have identified triplet vinylidene as an intermediate in the combination of triplet methylene, and in the photolysis of C_2H_2 , C_2H_4 , and C_2H_3Cl . During the past year we have completed a study of the photolysis of vinyl chloride. The photodecomposition may proceed by several paths:



Aside from C_2H_3 radicals, all decomposition products are readily discernable from their well-characterized VUV absorption features; reaction 1 is differentiable from reaction 2 by the temporal profile of C_2H_2 production even in the presence of the isomerization of $H_2C=C$. There was no evidence for Cl atom production and reaction 3 represents a minor process in the photodecomposition.

We found the time history of both $H_2C=C(^3B_2)$ and HCl to be identical which indicates they are both formed by a single process. HCl, a non-transient product, was determined directly from its absorption at 129 nm. At short times, following the incident flash, prior to any significant collisionally induced isomerization of the triplet $H_2C=C$, the concentrations of HCl and $H_2C=C$ are equal. As a result we have been able to derive the extinction coefficient for the 134 nm transition in $H_2C=C(^3B_2) = 694 \pm 218 \text{ cm}^{-1} \text{ atm}^{-1}$, base e.

While the direct observation of vinylidene is of great scientific interest, the importance of the radical in hydrocarbon chemistry remains unknown. The determination of the extinction coefficient permits a direct determination of the quantum yield for triplet vinylidene formation in the photolysis of C_2H_2 and C_2H_4 . In fact, $H_2C=C(^3B_2)$ formation represents major processes in both systems with quantum yields equal to 0.4 and 0.75, respectively. The photolysis of hydrocarbons control the atmospheres of the outer planets. Recognition of the important role of $H_2C=C(^3B_2)$ formation in these processes will have profound effects on models for these atmospheres.

We are in the process of determining quantitative quenching parameters of $H_2C=C(^3B_2)$ by Ar, N_2 , H_2 , CO, and CH_4 . In an earlier study it was shown that He quenched the deuterated vinylidene ($D_2C=C$) about 5.5 times slower than the protonated moiety. In the present work we have utilized that observation to increase the lifetime of the absorbing species and obtain rate data with greater precision and accuracy over longer times than if $H_2C=C$ were the reactive fragment.

The rate constants are the sum of all removal processes, including chemical interactions. In the case of H_2 and CH_4 we were unable to observe chemical reaction by end-product analysis, i.e., products derived from C_2H_3 or CH_3 radicals, respectively. The observation agrees with our earlier bond-strength-bond-length theoretical prediction of slow abstraction rate constants. For N_2 , there was no spectral evidence for HCN production. Overall rate constants, for the above species, are of the order $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In the coming year we will continue to investigate excited triplet vinylidene chemistry. We will search for other sources of the fragment and such chemical processes uniquely associated with excited triplet vinylidene. The flash photolysis-kinetic spectroscopy apparatus utilizes spectral detection technology that is out of date. We will upgrade the instrumentation with improved detection capability using array detectors. These offer the ability to record a large number of spectral elements which maintains the advantage inherent in plate technology, with photomultiplier sensitivity and speed without loss of spectral resolution.

3. Methods Development

(W. Braun, M. Hoffbauer, J. W. Hudgens, M. D. Scheer)

New technological developments offer many opportunities for the characterization of reactive systems and the generation of novel environments. The thrusts of our work involve the detection of reactive intermediates through multiphoton ionization and tandem mass spectrometry and the use of laser heating to study energy exchange effects. In each cases, a foundation has been laid for exciting future advances.

(a) Multiphoton Ionization Detection of Free Radicals
(J. W. Hudgens, M. Hoffbauer)

Resonance enhanced multiphoton ionization (REMPI) is a new method which probes the spectroscopy and dynamic properties of molecules. REMPI is a more universal detection method than laser excited fluorescence (LEF) since it does not require fluorescence from the probed species. As a result, REMPI will greatly expand the number of different chemical species that can be detected with lasers. Our efforts have concentrated upon free radical detection because the most important reactions in processes such as combustion, catalysis, and reactive etching involve free radicals. This work has been partially supported by the Army.

Multiphoton ionization works by subjecting molecules to intense visible or ultraviolet laser light that causes them to absorb photons until they ionize. Usually the first step features a simultaneous absorption of two or more photons which promotes the molecules into an excited electronic state. Then, the excited state molecule absorbs an additional photon and ionizes. Since ions are easy to detect, the technique is very sensitive.

During the past year the first phase of a laboratory for the detection of transient species was constructed. A significant effort was also expended designing future experimental apparatus. In addition to these activities, this year's research efforts produced manuscripts describing REMPI detection of benzyl radicals and SiF radicals.

Our experiments on benzyl radicals yielded the first successful REMPI detection of an aromatic free radical. Detection of aromatic free radicals using REMPI spectroscopy is an important goal since improved aromatic radical detection methods will allow studies that enable a better understanding of the reaction mechanisms important in the combustion of aromatic fuels.

In our experiments, benzyl radicals were generated in a flow reactor by reacting fluorine or chlorine atoms with toluene. The radicals effused into a mass spectrometer ion source where they were ionized by laser light tuned between 490-520 nm (Figure 1). The laser generated molecular ions were analyzed and detected by the mass spectrometer. The nature of the electronic state which facilitated the resonance enhancement was not ascertained, but resonance enhancement of the multiphoton ionization cross-section originated either from two photon resonances involving a Rydberg state, from two photon preparation of the 3^2B_2 state, or from three photon preparation of a Rydberg state associated with the second ionization potential. Future work will resolve this issue. Nevertheless, the detection sensitivity for benzyl radicals appears sufficient for use in kinetic experiments.

Silicon monofluoride, SiF, is a radical product from reactive etching of silicon surfaces. Its detection is of interest to the semiconductor industry. This year we studied its spectroscopy and reported two REMPI

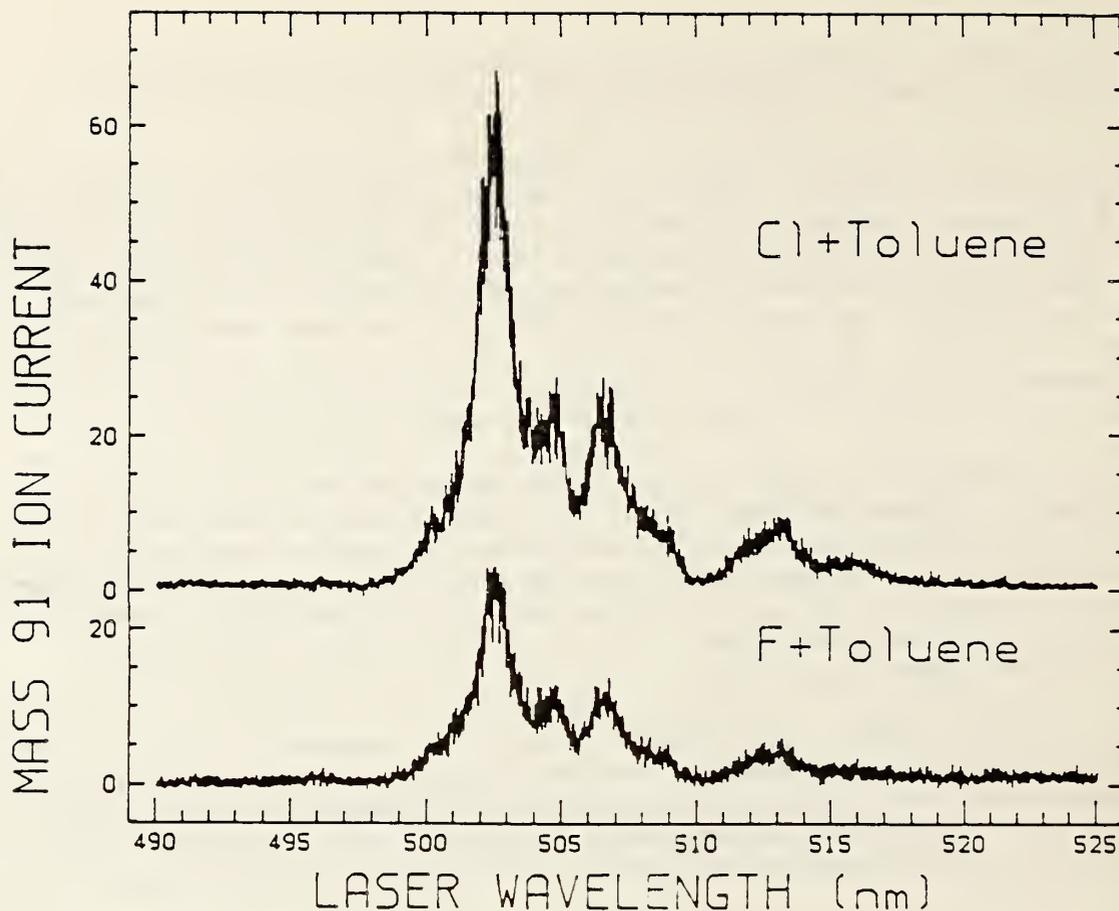


Fig. 1. The m/z 91 (Benzyl cation) signal observed from the flow reactor effluent as a function of dye laser wavelength (nm) between 490-525 nm for the reactions: a) F + toluene and b) Cl + toluene.

detection schemes. In both schemes SiF was ionized by absorption of three photons at wavelengths between 430-492 nm. One scheme involved two photon resonance enhancement from the $C' \ ^2\Pi_r + \ ^2\Pi_r$ bands. The second scheme used sequential one-photon steps between $(0,0) \ A \ ^2\Sigma^+ + \ ^2\Pi_{1/2}$ and $(1,0) \ C'' \ ^2\Sigma^+ + \ A \ ^2\Sigma^+$ transitions.

The works cited above are typical experiments used for the development of the REMPI radical detection data base. By generating a catalog of REMPI detectable species we can use selective and sensitive laser techniques to study problems which involve these radicals. We note that over the past year our earlier work on CH_3 and CH_2OH REMPI spectroscopy has enabled studies at other laboratories of hydrocarbon pyrolysis (Exxon), flame processes (NBS), photolysis (Yale, Cornell), and surface chemistry (Naval Research Laboratory). We believe the work described here will provide a similar stimulus.

This coming year phase two of the apparatus construction program will be largely completed. A paper describing the spectroscopy of CH_2F , CH and CF radicals observed during the reaction of $\text{F} + \text{Ketene}$ will be published and more detailed assignments of the resonant states of CH_2OH radicals will also be submitted. Laboratory work will target the generating reactions and spectroscopy of phenyl, vinoxy and vinyl radicals. Laser strategies used to selectively ionize these species may include two frequency MPI, production of doubly charged ions, and laser induced charge exchange schemes.

(b) Laser Heating
(W. Braun and M. D. Scheer)

Two separate projects have been pursued over the past year. These involved the further development of a high temperature furnace to study high temperature reaction kinetics and the development of a method to directly measure v-v and v-r, t energy transfer involving high energy species.

Many reaction processes either do not occur at low temperature or proceed so slowly that they cannot be conveniently measured. Two important cases are unimolecular bond scission and rearrangement reactions that require energies that exceed 50 kcal/mole. Historically, these reactions have been investigated either in conventional furnaces or in shock tubes employing chromatographic end-product detection. If a furnace can be designed such that high temperatures can be achieved for short residence times, then real-time measurements on stable products or reactive intermediates can isolate individual reaction steps and eliminate complicating and obscuring secondary reactions. Two papers have been published that have shown the feasibility of using a continuous wave IR laser heated reactor for mechanistic and activation energy studies. The first paper, "The Application of a New High Temperature Reactor to Unimolecular Decompositions" by M. D. Scheer, W. Braun, and J. R. McNesby describes the heating of fused silica by the absorption of laser infrared radiation as the basis for the design of a short residence time-high temperature reactor. When the laser is focused on the exit orifice of a silica flow tube a dilute mixture of a reactant gas in helium is exposed to the high orifice temperature for only about 2×10^{-5} s. During such short time intervals, secondary decompositions tend to be reduced. This heating method was applied to the multichannel decomposition of cyclobutanone. The formation of propylene by the secondary isomerization of cyclopropane was suppressed sufficiently and most of what was formed was shown to come directly from the cyclobutanone in a high activation energy dissociation channel.

"A New Comparative Method for the Determination of Activation Energies", by W. Braun and M. D. Scheer describes the use of the thermal radiation emitted by the surface of a rapid flow reactor as a reference standard in a new comparative method for determining chemical activation energies. The surface temperature, its thermal radiation, and the products formed in a reactive gas flowing through the reactor are all

modulated by the periodic on-off switching of a CO₂ laser that heats the reactor surface to incandescence. The activation energy may then be obtained from the energy of the thermal photons selected for observation and a comparison of the temperature dependence of the rate of product formation with that of the spectral radiance of the reactor surface at the chosen wavelength.

The direct energy transfer measurement consists of exciting vibrational energy in a molecule such as SF₆, SiF₄ or hexafluorobenzene. Using a translational energy monitor one can detect the energy flow from SF₆(v) to SF₆(r,t). Similarly using an internal (v) energy monitor such as toluene one can measure SF₆(v) + Tol(v') → SF₆(v'') + Tol(v'''). By setting up suitable microscopic phenomenological energy transfer mechanisms (equations) one can relate microscopic energy transfer parameters to macroscopic energy flow measurements. This in turn, will allow one to further distinguish the relative importance of v-v vs. v-r, t-v' processes. A publication describing the experimental method and the theory is presently in preparation.

(c) MS/MS Tandem Mass Spectrometry
(R.I. Martinez)

The focus of this study is the development of an analytical methodology to monitor directly in real-time, selected reactive polyatomic species in complex reacting mixtures. It is supported by the Air Force. The work will involve structural characterization of any component in a reaction mixture via MS/MS tandem mass spectrometry subsequent to the species-specific ionization of each component by "soft" 2-color multiphoton ionization (one wavelength used for up-pumping; a second wavelength used for ionization near threshold).

During the past year the specially-designed, modular MS/MS system has undergone extensive testing of all system and subsystem components (hardware and software). The breakdown of several critical components caused significant delays, and has necessitated extensive repairs and modification of the system hardware and software. Nonetheless, we were able to demonstrate the feasibility of coupling laser ionization to the MS/MS. Using tunable wavelengths between 277 nm (4.48 eV/photon) and 300 nm (4.13 eV/photon) to photoionize NH₃ (IP=10.16 eV), we observed NH₂⁺ (IP=11.4 eV; AP[NH₃]=15.7 eV) and NH⁺ (IP=13.1 eV; AP[NH₃]=17.1 eV). Moreover, the characterization of critical MS/MS control parameters to date supports the theoretical basis for the original design criteria, and suggests minimal fringing-field effects throughout the MS/MS. Relative to this, we installed variable rf-amplitude controllers for each quadrupole to allow independent control of the rf-amplitudes. This enables us to test theoretical concepts of acceptance/emittance through the tandem quadrupoles.

Work in FY86 will involve the measurement of CID breakdown curves for selected compounds, and development of 2-color MPI schemes for the same. These will be used in the study of oxidation reactions in flow reactors to be coupled to the MS/MS.

C. Condensed Phase Kinetics

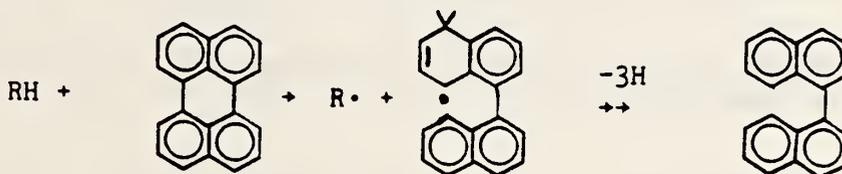
(R. L. Brown, R. Chen, L. Griffith, S. E. Stein and V. Senthilnathan)

This program represents one of the main thrusts of our competence program. We have found that aromatic condensation reactions, like their logical reverse reactions, ring-opening and desubstitution, are catalyzed by H-donors. A simple mechanism has been proposed for the former process and partly validated by experiment. Our work has also led to the first reported rate constants for a key hydrogen transfer step in liquid pyrolysis, transfer of an H-atom from a radical to a molecule. Our theoretical studies of large graphite-like molecules have systematically applied reliable organic theories to elucidate edge effects. This work provides details concerning the dominant role of edge structure in graphite chemistry discovered last year. Experimental studies are supported by the Gas Research Institute, theoretical studies by AFOSR.

1. Mechanistic Studies of Aromatic Pyrolysis

(R. Chen, V. Senthilnathan, S. E. Stein)

We are examining reactions in organic fluids at high temperatures with the aim of finding reaction pathways leading to polymerization and carbonization. We use this information to develop predictive theory. Over the past year a series of studies of the condensation of 1,1'-binaphthyl to perylene at 400°-560°C have been completed. This reaction is catalyzed by hydrogen donors and kinetic studies suggest the following mechanism,



This finding is counter to general experience in the area of carbonization chemistry where excess hydrogen leads to ring breakup. Rate parameters derived from these studies promise to provide a new means for obtaining free radical thermochemistry. We intend to determine the precise mechanism and rate limiting steps for several related condensation reactions next year.

2. Elementary Kinetic Studies of Polyaromatic Species in Solution

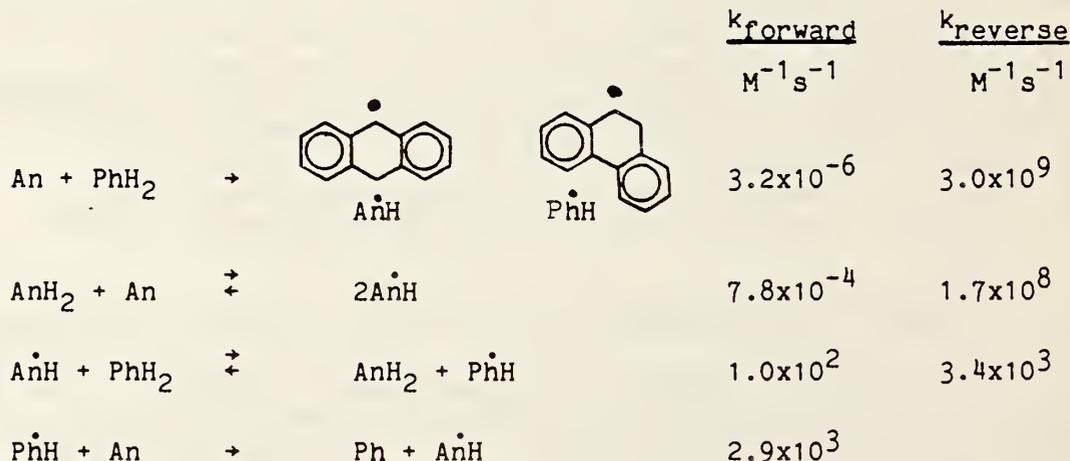
(R. L. Brown, L. Griffith, S. E. Stein)

These experiments are designed to yield rate constants and thermodynamics of elementary chemical reactions involving polyaromatic molecules and free radicals. Reactions are studied when they have been

identified as key processes in the thermal chemistry of aromatic substances and their rate constants are not available or reliably estimable. We have investigated the transfer of hydrogen from 9,10-dihydrophenanthrene to anthracene,



Kinetic studies at 350°C along with thermochemical kinetic analysis and computer modeling of results were used to derive the following mechanism and rate constants:



Especially noteworthy is reaction 4, an exothermic chain propagation step transferring a β -H atom from a radical to a molecule. It had been proposed but never unambiguously observed thermal chemistry prior to this work.

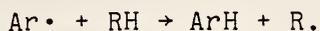
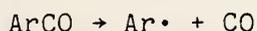
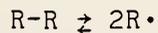
In other studies of H-transfer, we determined the rate of a similar, but thermoneutral reaction,



Assuming an A-factor of $10^{8.5} \text{ M}^{-1}\text{s}^{-1}$ we obtain an activation energy of 18 kcal mol⁻¹ for the reaction. This high value is consistent with the lack of prior kinetic data for these reactions; they are simply too slow to compete with other paths in most chemical systems. They are effective in our reaction systems because of the high concentrations of reactants and the lack of facile alternative pathways.

Next year we will attempt to measure rates of phenyl radical ()

and 1-naphthyl radicals () in high temperature fluids. Preliminary studies indicate that aryl aldehydes are very effective sources of such radicals. A mixture of bibenzyl (R-R, a radical initiator), toluene (RH, a radical trap) and an aldehyde has been found to provide an excellent means of generating these radicals at 300-400°C via the following mechanism,



3. ESR Detection of Aromatic Radicals at High Temperatures (R. L. Brown, M. Manka and S. E. Stein)

These experiments used our unique high temperature flow ESR instrument to investigate reactions of species large enough for steric effects to measurably influence their rates. Our goal is to separate the effects of steric and electronic factors on reaction rates to permit the development of more reliable predictive theory for large chemical species.

We have determined concentrations of diphenylmethyl radicals (D) in equilibrium with their dimer, 1, 1', 2, 2'-tetraphenylethane (DD) between 648 and 683K. Using previously measured rates for dissociation of DD we derived a rate constant for D recombination of $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 648K. This is markedly slower (a factor of ca. 6) than benzyl radical recombination under similar conditions, indicating a steric impediment to D recombination. An analysis of this data also indicates that the rate of DD dissociation was accelerated by a factor of ten by release of strain. This work provides unique quantitative data for species just large enough for strain to exert a measurable but not overwhelming influence on rates.

4. Graphite Properties (R. L. Brown and S. E. Stein)

In continuation of our work on the properties of very large polybenzenoid hydrocarbons, we have made a detailed study of the predictions which Huckel molecular orbital (HMO) theory makes for these molecules. HMO calculations yield orbital energies and wave functions for their pi-electrons. We have examined energy level densities, bond orders, electron distributions, free valence (a reactivity index), and resonance energies. Over thirty years ago, Coulson and Taylor [Proc. Phys. Soc. A65, 815 (1952)] applied HMO theory to graphite considered as an infinite, planar polybenzenoid molecule. They calculated the pi-electron energy per carbon, the density of states in the pi-electron band, and the pi-band order. We have been able to compare our calculations of these properties

for large finite-sized molecules with their limiting values. As in our previous work, four series of molecules, each with a different edge structure was considered.

The density of pi-states as a function of energy is shown in Figure 2 for a very large molecule having 2814 carbons and a phenanthrene type edge. The smooth curve shows the graphite limit calculated by Coulson and Taylor.

The orders of the bonds in the center of these molecules is given in Figure 3 as a function of molecular size (N_c = number of carbons). They clearly extrapolate to the graphite limit in each of the different series.

Hess and Schaad [J. Amer. Chem. Soc. 94, 3068 (1972)] have proposed a definition of resonance energy as the difference between the Huckel pi-electron energy and that of a particular reference structure which they define. Figure 4 shows the resonance energies per carbon for each of these series as a function of molecular size. They all extrapolate to the graphite limit although the series containing an anthracene type edges (series 1) experiences a deep minimum in resonance energy at about 400 carbons.

In graphite, the energy of the highest occupied molecular orbital (HOMO) is at the energy zero. For all of the series, the energies of the HOMO's extrapolate to zero. However, as shown in Figure 5, the rate of approach to this limit varies widely. Molecules with phenanthrene type edges (series 3) have HOMO levels which are particularly slow to approach zero. Since the pi-electrons in these top levels are the ones most likely to be involved in chemical reactions, this suggests the molecules having edges of the phenanthrene type would be relatively non-reactive until they reached a very large size.

These differences between the HOMO's of the different series are also quite evident in their pi-electron distributions. In the more reactive anthracene edge series, electrons in this top level are concentrated around the molecular perimeter while in the phenanthrene edge series these electrons are distributed more uniformly over the whole molecule. In the anthracene edge type, this concentration of electron density at the edge is not restricted to the top level only but extends downward some seven or so levels.

In the coming year we plan to consider strain and steric effects associated with edges and imperfections. Working models for chemical reactions of graphitic molecules will be devised.

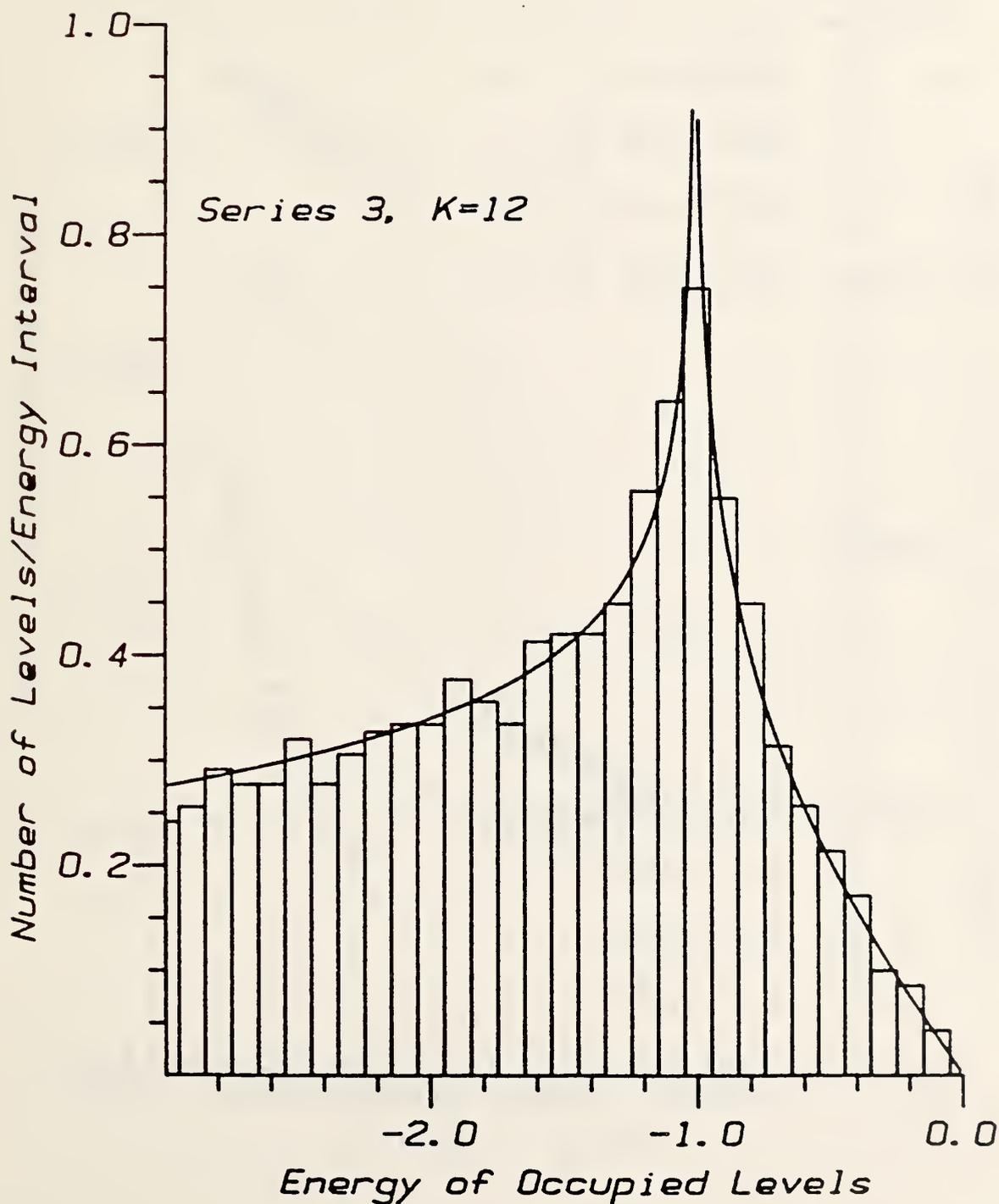


Fig. 2. Density of HMO orbital energy levels as a function of energy for molecule with 2814 carbons and a phenanthrene edge type. The smooth curve shows the graphite limit.

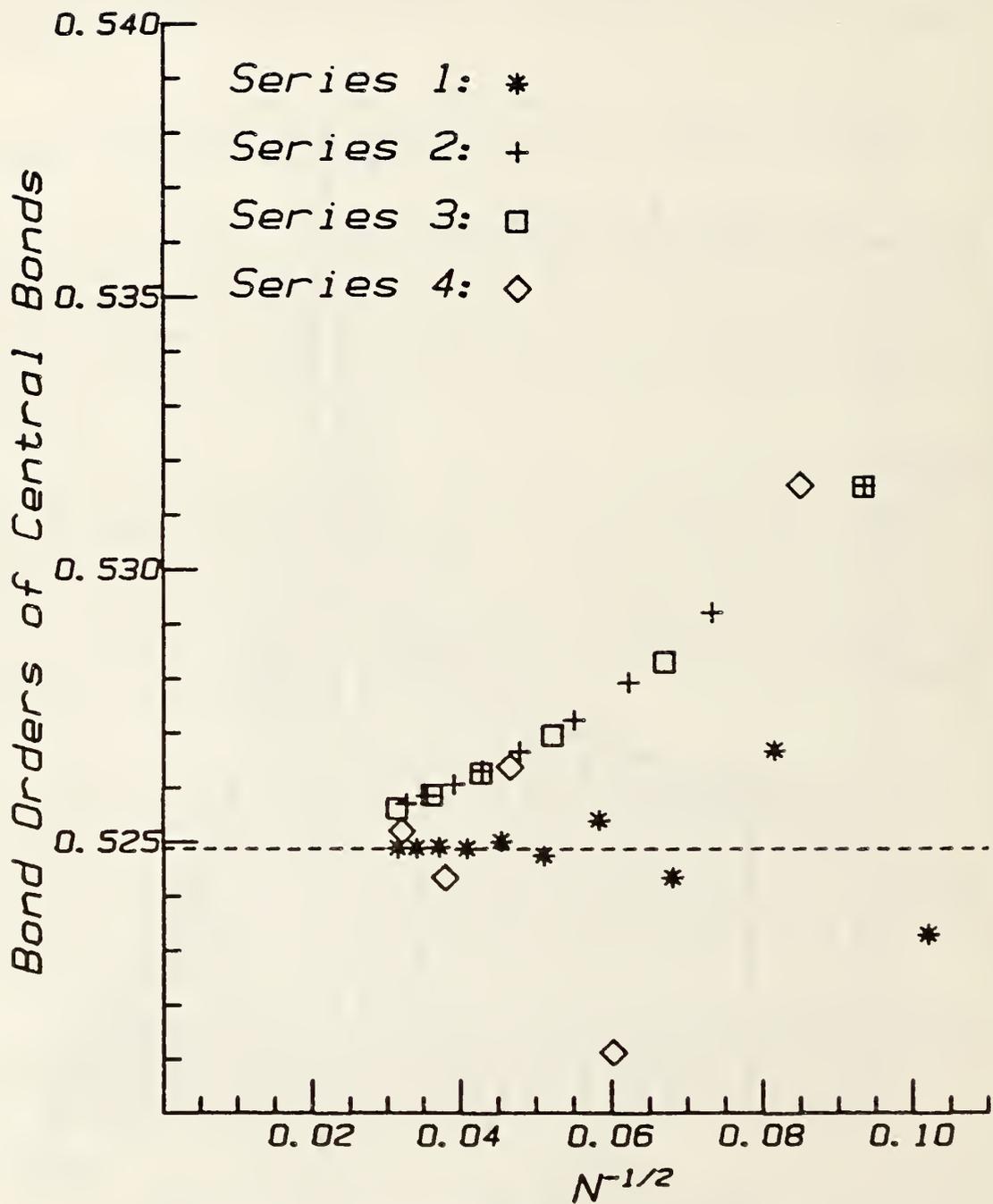


Fig. 3. Bond orders of bonds in centers of molecules in different homologous series as a function of molecular size. Dotted line shows graphite limit.

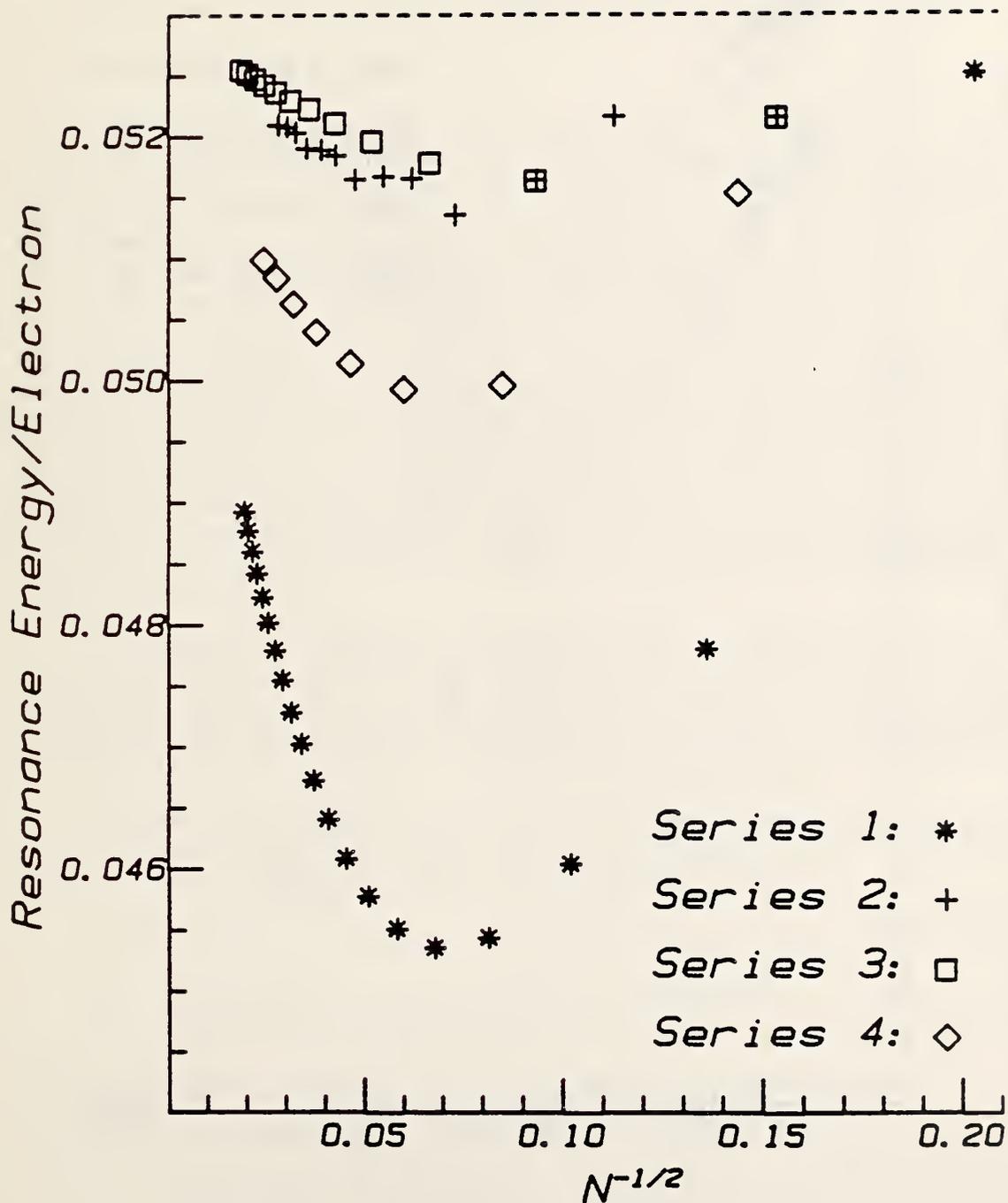


Fig. 4. Resonance energies per carbon as a function of molecular size. Dotted line shows graphite limit.

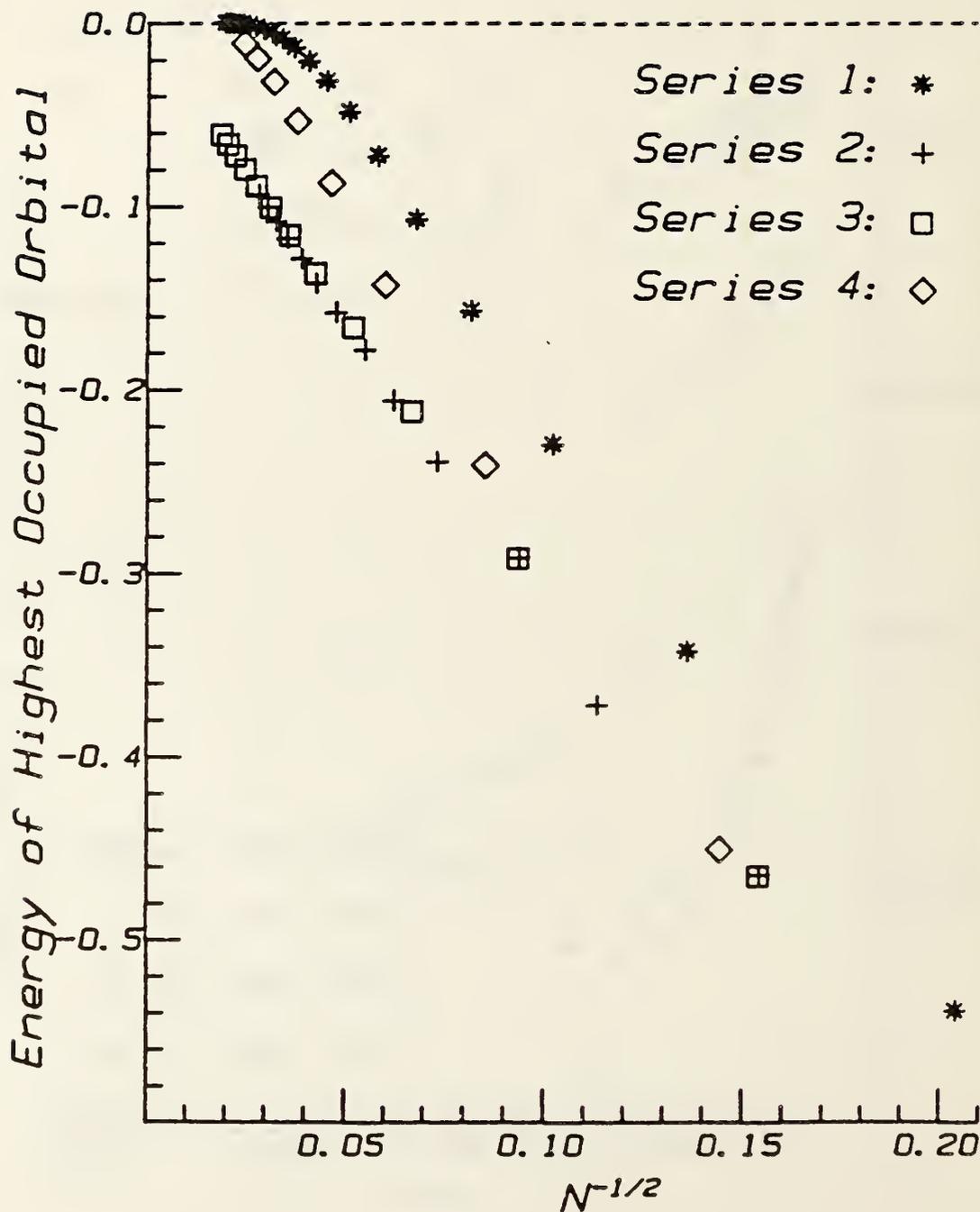


Fig. 5. Energy of highest occupied molecular orbital as a function of molecular size.

4. ION KINETICS

R. E. Huie, R. D. Levin, S. G. Lias, M. Mautner, P. Neta, I. Price
L. W. Sieck, Z. B. Alfassi, N. Altstein, A. Harriman, Z. Karpas
S. Mosseri, J. Rabani and M.-C. Richoux

A. Introduction

The scientific emphasis and focus of the work of the Ion Kinetics Group is derived largely from the competence-building program, "Kinetic Studies of the Effects of Ionizing Radiation". The Ion Kinetics Group was organized in 1979 under the direction of Dr. P. Ausloos to fulfill the requirements of this Competence. Originally called the Ionizing Radiation Group and assigned to the Chemical Thermodynamics Division, the nucleus of the group was transferred in 1983 to the Chemical Kinetics Division where the work on the kinetics of ionic processes became a natural complement to the existing programs on the kinetics of neutral species. The pre-existing Chemical Kinetics Division program on Aqueous Chemical Kinetics was incorporated as an integral part of the Liquid Phase Ion Kinetics activities. The group also has been historically affiliated with the Ion Kinetics and Energetics Data center, with members of the scientific staff collaborating on compilations and evaluations of data necessary to the understanding of the chemistry of ions and the effects of ionizing radiation on matter. The activities of the Data Center are described in Section 2.

The long range goal of our program "Kinetic Studies of the Effects of Ionizing Radiation" is to obtain experimental and theoretical results which contribute to the understanding of the response of matter to ionizing radiation in sufficient detail for application to radiation biology, radiation dosimetry and radiation processing.

The approach to the study of radiation effects involves diverse experimental tasks which examine individual facets of the problem area in detail. These individual tasks are summarized below:

Kinetics of the Interactions between Ions and Molecules

Fundamental investigations of the chemistry of ions, including elucidation of reaction rates, mechanisms and thermochemistry.

Energetics of Solvation and the Chemistry of Solvated Ions

Studies of the link between the kinetics and thermochemistry of ions in the gas phase and in the liquid phase; the prediction of liquid phase thermochemical parameters from the results of gas phase mass spectrometric studies.

Radiation Chemistry of Organic and Biochemical Solutions

Pulse radiolysis investigations into energy transfer and radiation damage mechanisms in biologically important substances.

Kinetics and Radiation Chemistry of Aqueous Inorganic Solutions

The study of electron transfer reactions in aqueous solutions of inorganic salts, with particular emphasis on the kinetics of reactions involving SO_3^- , SO_5^- , and HSO_5^- .

Ion Kinetics and Energetics Data Center

The maintenance of an up-to-date evaluated data base relating to the thermochemistry of ionization processes and the kinetics of ionic reactions, and the publication of related compilations.

The description of the scientific activities of the Group which follows will be organized under headings corresponding to the various activities listed above, although an arbitrary subdivision has been made between Gas Phase Ion Kinetics and Liquid Phase Ion Kinetics. Data Center activities are discussed in Section 2.

B. Gas Phase Ion Kinetics

The program aims at achieving a fundamental understanding of the unimolecular and bimolecular reactions of ionic species generated by high energy radiation, and further, at examining the effects of ion-molecule clustering, i.e., of solvation. Aspects of the program currently supported by the Department of Energy and the Air Force Office of Scientific Research give particular emphasis to examinations of processes involving small organic molecules, while experimental work tied in to the Liquid Phase Ion Kinetics effort (described below) focuses on model compounds which give information about processes in biochemical systems.

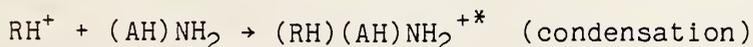
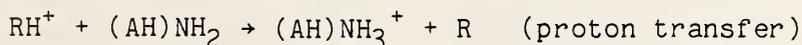
1. Kinetics of Ion-Molecule Reactions: Thermochemical Kinetics of Ions (S. G. Lias, M. Mautner, L. W. Sieck and Z. Karpas, in collaboration with P. Ausloos and T. J. Buckley)

Irradiation at energies above the ionization threshold produces positive ions which may undergo rapid ion-molecule reactions. This task involves the elucidation of the bimolecular chemistry of such ions, including an examination of reaction mechanisms, and measurements of rate constants and equilibrium constants as a function of temperature. The latter experiments lead to quantitative information about the thermochemistry of proton transfer, charge transfer, and other ionic reactions. Much of the work ties in directly with the work of the Ion Kinetics and Energetics Data Center. Accomplishments of the past year are discussed below.

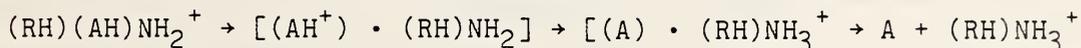
(a) In connection with an extensive evaluation of heats of formation of ions and of proton affinities of molecules being carried out this year in the Ion Kinetics and Energetics Data Center, a large number of proton affinity determinations have been accomplished (through equilibrium constant determinations or "bracketing" experiments) using the ion cyclotron resonance spectrometer. Species studied include selenium and tellurium compounds, and isocyanates, thiocyanates, and isothiocyanates. In a study of proton transfer from halogenated methyl ions, the first internally-consistent reliable heats of formation of the carbenes CF_2 , CCl_2 , $CFC1$, CFH , and $CClH$ were established.

(b) In exothermic charge transfer reactions of organic ions with organic molecules the possibility that a collision will be reactive is usually close to unity. However, charge transfer reactions in hydrazines have been shown to proceed with efficiencies as low as 0.001 to 0.1. In these reactions, the components undergo large geometry changes and it appears that these changes lead to significant barriers to reaction, which become smaller when the reaction is highly exothermic. Correspondingly, the rate constants increase with exothermicity. Steric effects are also observed in that cyclic reactants react faster than acyclic reactants.

(c) Several studies mapping mechanistic details of ion-molecule reactions have been completed. It was, for instance, demonstrated that in the reaction of alkyl ions, RH^+ , with alkylamines, $(AH)NH_2$, the branching ratio of the two competing channels,



remains constant from pressures of 10^{-6} torr to ~ 1 torr, a result which reflects the probabilities for different alkyl ion-amine configurations in the ion-molecule collision process. At low pressures it was demonstrated that the excited condensation ion, $(RH)(AH)NH_2^{+*}$, dissociates by cleavage of the weaker of the two N-C bonds to form an alkyl ion-amine complex, followed by proton transfer in the complex and dissociation:



In another investigation, it was shown that the reaction of the parent radical cations of halogen substituted alkanes with the respective parent molecules to form dialkyl halonium ions:

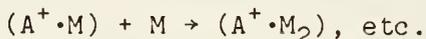


proceed through a classical S_N2 mechanism in which the halogen atom in the product ion originates entirely from the reactant neutral molecule. Earlier literature results had suggested that in the gas phase, the reaction proceeded through formation of a complex in which the halogen atoms were statistically distributed to the products.

(d) In a project sponsored by the Air Force Office of Scientific Research, the rates and mechanisms of consecutive ion-molecule reactions in styrene and phenylacetylene have been studied. A comprehensive examination of the structures and reaction kinetics of $C_6H_5^+$ ions is also being completed; it is found that structural assignments made in previous studies in the literature are in error. The photochemical dissociation mechanisms of the product condensation ions formed in most of these systems are currently being investigated using an argon ion laser as well as a xenon arc lamp fitted with interference filters as light sources.

2. Solvation Thermodynamics and the Kinetics of Solvated Ions (M. Mautner, L. W. Sieck)

Ionic species such as those generated in acidic or basic environments or by radiation are ubiquitous intermediates in biochemical and organic reactions. The stabilities and reactivities of ionic intermediates are affected by their intrinsic molecular properties (studied in the gas phase as described above), and by interactions with the condensed phase environment. This task utilizes the high pressure mass spectrometer to bridge the gap between the understanding of ionic chemistry attained in the gas phase studies and that required for understanding and prediction of processes occurring in irradiated liquids, acid-catalyzed reactions, and enzyme catalyzed processes. In the high pressure mass spectrometer, it is possible to generate a given ion in the presence of a solvent molecule (such as H_2O , for example) to determine the thermochemistry of solvation by an examination of equilibria such as:



and to study the kinetics and mechanisms of reactions of the solvated ions.

Work has been carried out during the past year on the following problems:

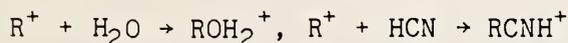
(a) Studies of ionic charge transfer complexes: Ionic states of aromatic molecules, such as benzene, substituted benzenes, or aniline and its derivatives are important in the radiation chemistry and electrochemistry of these compounds as well as in the conductivities of organic semiconductors. In these phenomena, the positively charged

radical ions interact with neutral molecules. The interaction can involve resonance charge transfer, i.e., stabilization of the complex by the resonance forms

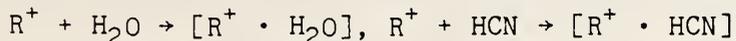


To understand the energetic effects of charge resonance, a study was conducted in collaboration with S. E.-Shall of Georgetown University of the complexes of the aniline radical cation with aniline derivatives and with aromatic hydrocarbons, as well as with other polar molecules. These studies were also complemented by Extended Hückel Molecular Orbital calculations. The results lead to the following conclusions: (1) Charge transfer (CT) resonance is most effective in complexes for which the ionization potentials of the components are equal. In these cases, charge transfer contributes 4 - 6 kcal/mol to the total binding energies of 16 - 20 kcal/mol of the complexes. (2) Charge transfer resonance is similar whether or not the charge on the components is delocalized or partially localized. (3) The most stable conformations of the complexes have parallel-plane sandwich type geometries. (4) With highly polar substituents such as -CN or -NO₂, the complexes rearrange to a linear geometry which is bonded by electrostatic interactions.

(b) In environments under irradiation, including planetary atmospheres, carbonium ions such as CH₃⁺ or more complex species, such as t-C₄H₉⁺ can associate with electron pair donors such as H₂O and HCN. These interactions could lead to covalently bonded protonated alcohols and nitriles:



However, the observed thermochemistry of some of the reactions, especially the entropy changes, indicates that the products are in some cases not covalent condensation products, but hydrogen-bonded complexes.



Both thermochemical arguments and collisional dissociation spectroscopy were used to show that the reactions result in the formation of the hydrogen bonded complexes. This may be important in planetary chemistry, since cluster formation will be an alternative route to the synthesis of higher molecular weight products by condensation.

(c) In acidic environments, amines and oxygen compounds are protonated to form the ions, BH⁺. These species are important in a range of phenomena from organic synthesis to enzyme reactions. The properties of these ions in water are strongly affected by solvation. To understand the details of ion solvation, data on ion clustering, which involves the first solvent shell, were analyzed. The results showed that enthalpies of hydration can be predicted from the thermochemistry of gas-phase ion-molecule clustering events. Further, it is possible to use the clustering data to analyze individual components of the heats of solvation

of ions, hydrogen bonding and bulk solvation terms (that is, cavity forming and dielectric charging terms). These terms show reasonable variation with the proton affinities and with the size of alkyl substituents of the ions.

(d) The stabilities of $\text{NO}_2^- \cdot \text{X}$ and $\text{C}_6\text{H}_5\text{NO}_2^- \cdot \text{X}$ association ions, where X was a dipolar protic or aprotic organic solvent, were investigated by pulsed high pressure mass spectrometry. By comparison, analogous measurements were made with Cl^- for certain model systems. Equilibrium constants were determined as a function of temperature in order to define ΔH and ΔS values for solvation. Solvation energies were found to vary as $\text{NO}_2^- \rightarrow \text{Cl}^- \rightarrow \text{C}_6\text{H}_5\text{NO}_2^-$ for ligands having -OH sites. Association entropies were found to be constant at -27 ± 2 for cluster ions incorporating NO_2^- or $\text{C}_6\text{H}_5\text{NO}_2^-$ and protic ligands, but vary significantly when Cl^- is the core ion. For aprotic ligands, such as $\text{X} = \text{CH}_3\text{CN}$, CH_3NO_2 , $(\text{CH}_3)_2\text{CO}$, etc., the values of $\Delta\text{H}_\text{D}^\circ$ and $\Delta\text{S}_\text{D}^\circ$ for both $\text{NO}_2^- \cdot \text{X}$ and $\text{C}_6\text{H}_5\text{NO}_2^- \cdot \text{X}$ were also found to exhibit large variations. Predictive correlations of $\Delta\text{H}_\text{D}^\circ$ as a function of gas phase acidity were developed. Differences in the various cluster stabilities are explicable in terms of the dipole accessibility of X. For example, the depressed $\Delta\text{H}_\text{D}^\circ$ values for CH_3CN and CH_3NO_2 can be interpreted in terms of the blocking effects of the methyl groups, which shield the group having most of the dipole moment of the ligand (-C+N, etc.). These measurements represent the first quantitative data ever gathered for gas phase association reactions involving complex anions and complex organic molecules.

(e) Another study funded by the Dept. of Energy involved association reactions of SF_6^- with H_2O , low molecular weight alcohols, and DMSO. $\Delta\text{H}_\text{D}^\circ$ values were found to be quite low, ranging from 10.0 kcal/mol for $\text{SF}_6^- \cdot t\text{-C}_4\text{H}_9\text{OH}$. As with NO_2^- , etc., the binding energies increase with the acid strength of the ligand. The hydrogen bond strengths are 3 kcal/mol lower than those found for $\text{C}_6\text{H}_5\text{NO}_2^-$ with common ligands, and essentially identical to, or slightly higher than, those reported elsewhere for clustering by I^- . Association reactions with simple carboxylic acids could not be investigated due to very efficient F^- transfer reactions yielding F^- (Acid)-type ions. An "effective" ionic radius of $\sim 2.1 \text{ \AA}$ was deduced for SF_6^- . These results provide a new insight into electrical breakdown mechanisms in SF_6 under conditions where it is used as a high pressure insulating gas.

C. Liquid Phase Ion Kinetics

1. Radiation Chemistry of Organic and Biochemical Solutions
(P. Neta, M.-C. Richoux, A. Harriman, M. Mautner, Z. B. Alfassi, S. Mosseri, and J. Rabani)

Pulse radiolytic techniques are used to characterize the chemical properties of short-lived species in irradiated solutions. Particular attention is given to reactions of reactive transients which have been implicated as intermediates in radiation-induced and thermal processes in a variety of chemical and biological systems. An important aspect of this program is the study of inter- and intramolecular electron transfer processes aimed at understanding similar phenomena in biological systems as well as in photochemical systems of interest for possible use in solar energy conversion; this aspect of the work is supported by the Department of Energy. By studying the kinetics and mechanisms of the various transient species and by understanding the parameters that control them, one can hope to be able to predict the behavior of these species in more complex systems.

(a) Photogeneration of oxygen from water is an integral part of green plant photosynthesis and many laboratory models aimed at the storage of solar energy have tried to mimic this natural process. In this problem area, an experimental examination of the catalytic oxidation of water to oxygen by metalloporphyrin pi-radical cations has been carried out. In the ideal case, a metalloporphyrin (synthetic analogue of chlorophyll) absorbs the light and forms an excited state which then donates an electron to another compound in the system. The electron acceptor then reacts with a catalyst to form hydrogen from water. The metalloporphyrin radical-cation (formed after donating an electron) should react with another catalyst that will produce hydrogen (a fuel) and oxygen by sunlight with no net change in the other components of the system. For this purpose, it is necessary to find the proper catalyst, the best metalloporphyrin, and the optimal experimental conditions for oxygen production. This was done using pulse radiolysis and monitoring the rate of reaction of various porphyrins and catalysts to determine the factors that influence these rates. With this approach, a tedious search for oxygen product under different conditions was unnecessary. After optimization of the kinetic factors by pulse radiolysis, it was found that the optimal kinetic conditions also gave the highest oxygen yield.

Last year's experiments with several zinc porphyrins showed that although all the porphyrins examined had sufficiently high oxidation potentials so that their radical cations could oxidize water to oxygen, their efficiencies were determined to a large extent by the lifetime of the cations, i.e. kinetic parameters were more important than thermodynamics. Therefore, a search for porphyrins with longer-lived radical cations was continued. It was found that at high pH, zinc p-tetrahydroxyphenylporphyrin formed a very long-lived radical cation, but that reaction with the RuO_2 catalyst for water oxidation was inefficient because the redox potential of this porphyrin at high pH was too low. An examination of the oxidation of magnesium tetrasulfonatophenylporphyrin (MgTPPS) showed the formation of a stable radical cation which was able to oxidize water to oxygen on RuO_2 catalyst only at very high pH values. Another approach to the problem is to utilize metalloporphyrins in which the metal is oxidized rather than the ligand. Experiments with PbII-porphyrins indicated two stage oxidation to the radical cation and

then to the PbIV-porphyrin. The latter product was unstable over long times and its decay was hardly affected by the presence of the RuO₂ catalyst, i.e. it was not found suitable for efficient oxidation of water. Preliminary experiments with MnIII-porphyrins showed that the MnIV-porphyrins produced upon oxidation decay in a pH dependent process and their decay was accelerated by the addition of RuO₂. The pH profile of the reaction with the catalyst and oxygen production is currently under study.

Since the probability of reaction with the catalyst is found to be greatly dependent on the lifetime of the porphyrin radicals, a systematic examination of the parameters that affect the lifetimes was initiated. A study of various metalloporphyrin radical anions indicated dependence of the lifetime on the electronegativity of the metal, which affects also the reduction potential of the porphyrin. This was rationalized on the basis of electron-withdrawing by the metal center from the porphyrin ligand radical anion, which inhibits protonation of this anion in water. The rate and extent of protonation was found to affect the decay very strongly. A systematic study on porphyrin radical cations has been initiated.

After completion of the study on the stability of radical cations and the catalyzed decay of MgTPPS.+ and of the MnIV-porphyrins, the basic redox chemistry of other metalloporphyrins will be examined, and the possibility of utilizing them in the photodecomposition of water will be explored. To further improve the efficiency of reaction of porphyrin radical cations with catalysts, micelles and polyelectrolytes will be utilized to extend the lifetimes of the radical cations.

With relation to the use of polyelectrolytes in solar energy conversion systems, the possibility of using radiation to bind ruthenium trisbipyridyl covalently to several polyelectrolytes has been explored. It was found that if OH radicals are allowed to react partially with the Ru(bpy)₃ and partially with the polyelectrolyte, the two types of radicals react to a large extent to form new covalent bonds. The irradiated polyelectrolyte was indeed found to have the complex bound to it.

(b) The toxicity of halogenated alkanes (such as carbon tetrachloride and the anaesthetic agent halothane, CF₃CHClBr) is believed to originate from cytochrome-P₄₅₀-mediated generation of peroxy radicals with subsequent attack on biological targets, especially unsaturated lipids. The feasibility of this proposed mechanism was demonstrated last year in this laboratory in a pulse radiolytic study of the reactions of peroxy radicals with iron porphyrins and with fatty acids using Fe^{III}-deuteroporphyrin as a model for cytochrome P₄₅₀. Peroxy radicals derived from the halogenated hydrocarbons were found to oxidize the ferric porphyrin by an electron transfer mechanism to product a Fe^{III}-porphyrin pi-radical cation. In the continued investigation of this problem area, the reaction of peroxy radicals derived from methanol and isopropanol with FeIII-porphyrins was found from kinetic studies to involve the formation of an intermediate complex which decomposes to final products in acid-dependent and acid-independent processes. This may suggest that all

reactions of peroxy radicals with porphyrins involve an intermediate complex. To further understand the behavior of peroxy radicals, a kinetic study of their reactions with other porphyrins in a variety of solvents, and with other organic reactants has been initiated.

(c) A focus of the on-going program of study of intramolecular electron transfer processes is the investigation of temperature effects on such processes. Studies were carried out on nitroaromatic halides in which electron attachment on the nitro group is followed by electron transfer through the molecule leading to halide loss. Earlier work had demonstrated that the rate of the intramolecular electron transfer depends on the respective geometries of the nitro and halide functions in the molecule. Since the dependence of the rate constants on molecular geometry is governed by energy barriers and entropies of activation, a physical understanding of structural effects can be achieved only if both of these factors are known, i.e. if the rate constants are known as a function of temperature. Using the temperature-controlled pulse radiolysis cell, a series of reactions were examined. The results show that both the energy barriers and the entropies of activation vary significantly from reaction to reaction. Some specific structural trends emerge, such as the decrease of reaction probabilities when steric factors interfere with optimal orientation of the substituents for electron transfer.

Other intramolecular interactions examined were those in dimeric viologens. A series of compounds was synthesized having two identical viologen groups separated by organic bridges of varying degree of flexibility. Chemical or radiolytic reduction results in formation of the viologen radicals which undergo disproportionation to form the doubly reduced viologen. In this species, both viologen units are reduced to the radical and there is a distinct stabilization effect if the molecule can form an intramolecular cofacial dimer. The mono radical could be stabilized by intramolecular association with the unreduced viologen. This is achieved by fairly slow conformational rearrangement and it is in competition with bimolecular electron transfer to the preferred conformation. All the mono radicals disproportionate and the bimolecular rate constants have been measured. This study will be extended to mixed viologen dimers in order to examine the possibility of intramolecular electron transfer. Similar experiments are planned also with dimeric porphyrins and mixed porphyrin-viologen dimers. The purpose of this work is to achieve an understanding of similar natural processes, occurring for example during photosynthesis, with the hope of synthesizing a model that will mimic the natural process effectively.

(d) In order to determine the enthalpy and entropy changes that contribute to the electron affinities of organic and biological molecules in aqueous solution, the temperature dependences of charge transfer equilibrium constants in the pulse radiolysis of liquids was studied using the temperature-controlled pulse radiolysis cell. Preliminary results show that the major differences between molecular electron affinities are due to enthalpy effects, but in large molecules entropy effects are also

significant. This is of interest to biological systems related to the action of quinone containing co-enzymes, which are large molecules and which participate in biological electron transfer processes.

2. Kinetics and Radiation Chemistry of Aqueous Inorganic Solutions
(R. E. Huie and P. Neta in collaboration with P. A. Ouellette)

The current experimental work in aqueous phase chemical kinetics is an outgrowth of an effort to understand the mechanism for formation of acid rain, with particular emphasis on the chemistry of the key intermediates SO_3^- , SO_5^- , and peroxymonosulfate, HSO_5^- . Work in this problem area is now being supported by a contract with the EPA. Under this contract, several free radical reactions involved in the aqueous-phase oxidation of (IV) are to be investigated along with reactions of NO_3 .

In this work, pulse radiolysis is used as a technique to selectively generate reactive intermediate species of interest. Stopped flow and kinetic spectrophotometry experiments are performed to obtain complementary information on aqueous kinetics.

(a) During the past year, the initial thrust of the experimental effort to establish the basic reactivity of the radicals SO_3^- and SO_5^- was completed with the study of the reactions of these radicals with a series of phenolic compounds. The mutual effect of hydroquinone and sulfite on each other's autoxidation has been known for a century. It was apparent very early that this was due to interference with the free radical chain reactions involved in autoxidation. In order to understand better the mechanism of the autoxidation of sulfite solutions and the chemical effects associated with this phenomenon, the rates of the reactions of SO_3^- and SO_5^- with hydroquinone and other hydroxyphenols, and of sulfite with some phenoxyl radicals, were determined. The rate constants for the oxidation of hydroxyphenols by SO_3^- were small in neutral solution, but increased dramatically in basic solution as the hydroxyphenol was deprotonated. The SO_5^- radical reacts with most hydroxyphenols at moderate rates in neutral solution. Phenoxyl radicals with high redox potentials (phenol, resorcinol, and chloroglucinol) were found to oxidize sulfite in neutral solution.

(b) Few quantitative data exist on the electron transfer reactions of the radicals NO_2 , ClO_2 , and peroxy radicals, although these species are of considerable importance in many fields of chemistry. Systematic studies aimed at determining these rate constants have been initiated. Rate constants for the oxidation of ClO_2^- and NO_2^- by several organic and inorganic free radicals along with rate constants for several reactions of ClO_2 , NO_2 , and BrO_2 have been determined. Also, equilibrium constants have been determined for the reactions of ClO_2 with aniline at pH 6.9 and N,N-dimethylaniline at pH 9.6, leading to redox potentials at these pH's of 1.03 V and 0.87 V for the aromatic amines. From the rate constants for the reactions of ClO_2 and NO_2 with ferrocyanide, a ratio of self-exchange rates for these radicals was derived which is consistent

with that derived from the rate constants for the oxidation of ClO_2^- and NO_2^- by several substitution-inert transition metal complexes. From the rate constants for the reactions of these radicals with several organic compounds, a substantially different value was derived, due to a much higher apparent self-exchange rate for the $\text{NO}_2/\text{NO}_2^-$ couple.

(c) The NO_3 radical may be of considerable importance as a radical initiator in the aqueous chemistry of the atmosphere. A study of the chemistry of this species has been made using the pulse radiolysis of 6 M nitric acid to generate the radical. The rate constants for the reactions of NO_3 with several organic and inorganic reactants have been determined. It is seen that NO_3 is a strong oxidant with a one-electron oxidation potential greater than 2 V.

(d) The reactions of ferrous ions with peroxymonosulfate have been studied using the stopped-flow method using both excess ferrous and excess peroxymonosulfate. In both cases, the reaction did not show simple second-order behavior. At low concentrations, the first-order rate constant increased normally with the concentration of the reagent in excess. As the concentration of this reagent increased further, however, the first-order rate constant approached a plateau, suggesting that the reaction involves the initial formation of a complex which dissociates to the ferric product (and a free radical which rapidly oxidizes a second ferrous ion). The formation of the complex is the rate-limiting step at low concentration, while its dissociation is rate-limiting at high concentration. These data are presently being analyzed in collaboration with Dr. N. C. Peterson of the Polytechnic Institute of N.Y. to extract the rate constants for the individual steps.

(a) Publications of Past Year

- Baral, S., Hambright, P., Harriman, A. and Neta, P., "Radiolytic Studies of the Redox Reactions and Alkylation of Rhodium Tetrakis (4-Sulfonatophenyl) Porphyrin in Aqueous Solution", *J. Phys. Chem.*, 89, 2037 (1985).
- Baral, S., Neta, P. and Hambright, P., "Spectrophotometric and Kinetic Studies of the Radiolytic Reduction of Several Pyridylporphyrins and their Metal Complexes", *Radiat. Phys. Chem.*, 24, 245 (1984).
- Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., Troe, J. and Watson, R. T., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement II", CODATA Task Group on Chemical Kinetics, *J. Phys. Chem. Ref. Data*, 13 (#4), 1259-1380 (1984).
- Billmers, R., Griffith, L. L. and Stein, S. E., "Hydrogen Transfer Between Anthracene Molecules", *ACS Fuel Div. Preprints*, 30(4), 283 (1985)
- Braun, W. and Scheer, M. D., "A New Comparative Method for the Determination of Activation Energies", *Chem. Phys. Letters*, 118, 229 (1985).
- Brown, R. L., "Modeling of Axially Symmetric Flow Reactors", *Computers and Chemistry*, 8, 139 (1984).
- Buckley, T. J., Sieck, L. W., Metz, R., Lias, S. G. and Liebman, J. F., "Consecutive Ion-Molecule Condensation Reactions and Photodissociation Mechanisms of Condensation Ions in Polyacetylenic Compounds", *Int. J. Mass Spectrom. Ion Phys.*, 65, 181 (1985).
- Carlson, B. W., Miller, L. L., Neta, P. and Grodkowski, "Oxidation of NADH Involving Rate-Limiting One-Electron Transfer", *J. Am. Chem. Soc.*, 106, 7233 (1984).
- Christensen, P. A., Harriman, A., Porter, G. and Neta, P., "Metalloporphyrin and Photochemical Study of the Oxidation of Water by Zinc Porphyrin π -Radical Cations", *J. Chem. Soc. Faraday Trans. 2*, 80, 1451 (1984).
- DeMore, W. B., Golden, D. M., Hampson, R. F., Howard, C. J., Kurylo, M. J., Margitan, J. J., Molina, M. J., Ravishankara, A. R. and Watson, R. T., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, "Evaluation No. 7 of the NASA Panel for Data Evaluation, JPL Publication 85-37, Jet Propulsion Laboratory, Pasadena, CA, July, 1985.
- Duignan, M. T. and Hudgens, J. W., "Multiphoton Ionization Spectroscopy of ClO and BrO Radicals", *J. Chem. Phys.*, 82, 4426 (1985).
- Dulcey, C. S. and Hudgens, J. W., "Detection of SiF Radicals by Multiphoton Ionization Spectroscopy", 118, 444 (1985).

- Fahr, A. and Laufer, A. H., "Photodissociation of Vinyl Chloride: Formation and Kinetics of Vinylidene- $\text{H}_2\text{CC}(^3\text{B}_2)$ ", J. Phys. Chem., 89, 2906 (1985).
- Fahr, A. and Laufer, A. H., "Extinction Coefficient of $\text{H}_2\text{CC}(^3\text{B}_2)$ at 137 nm", J. Chem. Phys., 83, 908 (1985).
- Greenberg, A., Stein, S. E. and Brown, R. L., "Relative Thermochemical Stabilities and Reactivities of Benzo[a]pyrene and Selected Isomers", The Science of the Total Environment, 40, 219 (1984).
- Grodkowski, J., Jr., Chambers, J. H. and Neta, P., "Kinetics of Electron Transfer from Cobalt(II)-Porphyrins to Various Metalloporphyrin π -Radical Cations in Irradiated Carbon Tetrachloride Solutions", J. Phys. Chem., 88, 5332 (1984).
- Grodkowski, J., Neta, P., Schlesener, C. J. and Kochi, J. K., "Rates and Mechanisms of Reduction of Trisphenanthroline-Fe(III) by Various Radicals. Effect of Solvent", J. Phys. Chem., 89, 4373 (1985).
- Gupta, R. P., Larroquette, C. A., Agrawal, K. C., Grodkowski, J. and Neta, P., "Potential Radiosensitizing Agents. 7. (4(5)-iodo-5(4)-Nitroimidazole Derivatives", J. Med. Chem., 28, 987 (1985).
- Harriman, A., Christensen, P. A., Neta, P. and Richoux, M. C., "Metalloporphyrin Photosensitized Oxidation of Water", Sci. Papers Inst. Phys. Chem. Res. (Japan) 78, 143 (1984).
- Hudgens, J. W. and Dulcey, C. S., "Observation of the $3s^2A$ Rydberg States of Allyl and 2-Methylallyl Radicals with Multiphoton Ionization Spectroscopy", J. Phys. Chem., 89, 1505 (1985).
- Huie, R. E. and Neta, P., "The Chemical Behavior of SO_3^- and SO_5^- Radicals in Aqueous Solutions", J. Phys. Chem., 88, 5665 (1984).
- Huie, R. E. and Neta, P., "Reaction of the Vanadate Ion with Chlorpromazine and the Chlorpromazine Free Radical with Vanadyl Ion", Inorg., Chem., Acta., 93, L27 (1984).
- Huie, R. E. and Neta, P., "Oxidation of Ascorbate and a Tocopherol Analogue by the Sulfite Derived Radicals SO_3^- and SO_5^- ", Chem. Biol. Interactions, 53, 233 (1985).
- Huie, R. E. and Neta, P., "One-Electron Redox Reactions in Aqueous Solutions of Sulfite with Hydroquinone and other Hydroxyphenols", J. Phys. Chem., 89, 3918 (1985).
- Infante, G. A., Guzman, P., Alvarez, R., Figueroa, A., Correa, J. N., Myers, J. A., Lanier, L. J., Williams, T. M., Burgos, S., Vera, J. and Neta, P., "Radiosensitization by Derivatives of Isoindole-4,7-dione", Radiat. Res., 98, 234 (1984).
- Laufer, A. H., "Vinylidene ($^3\text{B}_2$) - An Active Intermediate in the Photolysis of Ethylene", J. Photochem., 27, 267 (1984).

- Lias, S. G., Liebman, J. F. and Levin, R. D., "Evaluated Gas Phase Basicities and Proton Affinities of Molecules: Heats of Formation of Protonated Molecules", J. Phys. Chem. Ref. Data, 13, 695 (1984).
- Lias, S. G., "Thermoneutral Isotope Exchange Reactions in Proton-Bound Complexes of Water with Organic Molecules: Correlations with Energetics of Formation of the Corresponding Association Ions", J. Phys. Chem., 88, 4401 (1984).
- Lias, S. G., Jackson, J.-A.A., Argentar, H. and Liebman, J. F., "Substituted N, N-Dialkyl Anilines: Relative Ionization Energies and Proton Affinities through Determination of Ion-Molecule Reaction Equilibrium Constants", J. Org. Chem., 50, 333 (1985).
- Lias, S. G. and Ausloos, P. J., "Structures of $C_6H_7^+$ Ions Formed in Unimolecular and Bimolecular Reactions", J. Chem. Phys., 82, 3613 (1985).
- Meot-Ner (Mautner), M., Nelsen, S. F., Willi, M. F., Frigo, T. B., Effects of an Unusually Large Neutral to Radical Ion Geometry Change: Adiabatic Ionization Energies and Proton Affinities of Alkylhydrazines", J. Am. Chem. Soc., 106, 7684 (1984).
- Meot-Ner (Mautner), M. and Deakyne, C. A., "Unconventional Ionic Hydrogen Bonds. 1. $CH^+ \cdots X$. Complexes of Quaternary Ions with n- and π -Donors", J. Am. Chem. Soc., 107, 469 (1985).
- Meot-Ner (Mautner), M. and Deakyne, C. A., "Unconventional Ionic Hydrogen Bonds. 2. $NH^+ \cdots \pi$. Complexes of Onium with Olefins and Benzene Derivatives", J. Am. Chem. Soc. 107, 474 (1985).
- Meot-Ner (Mautner), M., Ross, M. M. and Campana, J. E., "Stable Hydrogen Bonded Isomers of Covalent Ions", J. Am. Chem. Soc., 107, 4835 (1985).
- Morehouse, K. M. and Neta, P., "Kinetics of Demetallation of Manganese(II)-Porphyrins in Aqueous Solutions", J. Phys. Chem., 88, 3118 (1984).
- Neta, P., Dizdaroglu, M. and Simic, M. G., "Radiolytic Studies of the Cumyloxyl Radical in Aqueous Solutions", Israel J. Chem., 24, 25 (1984).
- Neta, P. and Simic, M. G., "Free Radical Chemistry of Natural Products", Proc. IFT Basic Symposium on Chemical Changes in Food Processing, 63 (1984).
- Neta, P. and Huie, R. E., "One-Electron Redox Reactions Involving Sulfite Ions and Aromatic Amines", J. Phys. Chem., 89, 1783 (1985).
- Neta, P. and Harriman, A., "Zinc Porphyrin π -Radical Cations in Aqueous Solution. Formation, Spectra and Decay Kinetics", J. Chem. Soc. Faraday Trans. II, 81, 123 (1985).

- Neta, P., Richoux, M. C. and Harriman, A., "Intramolecular Association of Covalently-Linked Viologen Radicals", J. Chem. Soc. Faraday Trans. 2, 81, 1427 (1985).
- Scheer, M. D., "A Kinetic Isotope Effect in the Thermal Dehydration of Cellobiose", in "Fundamentals of Thermochemical Biomass Conversion", Elsevier Applied Science Publishers, London and New York, 1985, pp. 89-95.
- Scheer, M. D., Braun, W. and McNesby, J. R., "The Application of a New High Temperature Reactor to Unimolecular Decomposition", Chem. Phys. Letters, 113, 407 (1985).
- Schwarz, F. P., Okabe, H. and Ausloos, P., "Pulse Radiolysis of Hexafluorobenzene: Production and Quenching of $C_6F_6^+(B)$ ", Chem. Phys. Lett., 119, 188, (1985).
- Schwarz, F. P. and Smith, D., "The Yields of Excited States of Aromatic Derivatives in the Radiolysis of Hydrocarbon Solutions", Radiat. Phys. Chem., Vol. 26, No. 3, 257-266, 1985.
- Schwarz, F. P., "Positive Charge Transfer in the UV Photolysis and β Radiolysis of Trans-Decalin Solutions", Radiat. Phys. Chem., Vol. 2, No. 3, 401-413, 1985.
- Shaub, W. and Tsang, W., "Overview of Dioxin Formation in Gas and Solid Phases Under Municipal Incinerator Conditions" in "Chlorinated Dioxins and Dibenzofurans in the Total Environment", L. H. Keith, C. Ruppe and G. Choudhery, ed., Butterworth, London, England, 1985, p. 469.
- Sieck, L. W. and Meot-Ner (Mautner), M., "Thermal Decomposition of Ions. 1. Pyrolysis of Protonated Ethers-Activation Energies and A Factors", J. Phys. Chem. 88, 5324 (1984).
- Sieck, L. W. and Meot-Ner (Mautner), M., "Thermal Decomposition of Ions. 2. Pyrolysis of Protonated t-Butyl Methylether at the Pressure Limit. Activation Efficiencies for Various Bath Gases", J. Phys. Chem., 88, 5328 (1984).
- Stein, S. E. and Manka, M., "Disproportionation-Recombination Rate Ratios of Hydroaromatic Radicals", J. Phys. Chem., 88, 5914 (1984).
- Stein, S. E., Brown, R. L., Griffith, L. L. and Manka, M., "Chemical Fundamentals of Coal Char Formation", ACS Div. Fuel Chem. Preprints, 29(2), 42 (1984).
- Stein, S. E., "Free Radicals in Coal Conversion", in "Coal Conversion Chemistry", R. D. Schlosberg, ed., Pergamon Press, 1985, pp. 13-44.
- Stein, S. E. and R. L. Brown, "Chemical Theory of Graphite", Carbon, 23, 105 (1985).

- Stein, S. E. and Fahr, A., "High Temperature Stabilities of Hydrocarbons", J. Phys. Chem., 89, 3714 (1985).
- Tsang, W., "Single Pulse Shock Tube Studies of the Thermal Stability of Ketones", Int. J. Chem. Kin., 16, 1543, (1984).
- Tsang, W., "The Stability of Alkyl Radicals", J. Am. Chem. Soc., 107, 2873, (1985).
- Tsang, W. and Hampson, R. F., "Chemical Kinetic Data Base for Methane Combustion", NBSIR 84-2913, June, 1985
- Tsang, W., Macek, A., Domalski, E., Walker, J. A., Charagundl, S. R., Colbert, J. C., Kirklin, D. R., Ledford, A. E., Dekker, P. H. and Ryan, R. V., "Combustion Characteristics of Refuse Derived Fuels", NBSIR, 83-1343, 1985.
- Tsang, W. and Walker, J. A., "Chemical Processes During the Starved Air Incineration of Municipal Solid Waste", NBSIR 84-2938, 1985.

(b) Publications in Progress.

- Ausloos, P. and Lias, S. G., "On the Mechanism of the Reactions of Alkyl Ions with Alkylamines: Competing Proton Transfer and Condensation Reactions", J. Am. Chem. Soc. (in press).
- Billmers, R., Griffith, L. L. and Stein, S. E., "Hydrogen Transfer Between Anthracene Structures", J. Phys. Chem. (in press).
- Brault, D. and Neta, P., "Oxidation of Fe^{III}-Porphyrins by Peroxyl Radicals Derived from 2-Propanol and Methanol - Evidence for Acid Dependent and Acid Independent Pathways", Chem. Phys. Letters (in press).
- Brault, D., Neta, P. and Patterson, L. K., "The Liquid Peroxidation Model for Halogenated Hydrocarbon Toxicity. Kinetics of Peroxyl Radical Processes Involving Fatty Acids and Fe(II)-Porphyrins", Chem. Biol. Interact. (in press).
- Brown, R. L., "Application of Semi-Empirical SCF-MO Theory to Very Large Hexagonally Symmetric Benzenoid Polyaromatic Hydrocarbons", NBSIR (submitted).
- Christensen, P. A., Harriman, A., Neta, P. and Richoux, M. C., "Photooxidation of Water Using Prussian Blue as Catalyst", J. Chem. Soc. (in press).
- Davis, C., Braun, W., Cvetanovic, R. J. and Tulloch, J., "Studies of Infrared Laser Heating of Polyatomic Gases by Optical Heterodyne Techniques", in "Lasers as Reactants and Probes in Chemistry", Howard University Press, (in press).
- Deakyne, C. A., Meot-Ner (Mautner), M., Campbell, C. L., Hughes, M. G., Murphy, S. P., "The Proton in Multisolvant Clusters. 1. The Acetonitrile-Water System", J. Chem. Phys. (in press).
- Dixon, D. A. and Lias, S. G., "Absolute Value of Gas Phase Proton Affinities and Basicities of Molecules: A Comparison Between Theory and Experiment", in "Molecular Structure and Energetics", J. F. Liebman and A. Greenberg, ed. (in press).
- El-Shall, M. S. and Meot-Ner (Mautner), M., "Ionic Charge Transfer Complexes. 2. Localized Acceptors Delocalized Donors: Complexes of Aniline with Aromatic Hydrocarbons", J. Am. Chem. Soc. (submitted).
- Fahr, A. and Laufer, A. H., "Primary Processes in the Photochemistry of Simple Hydrocarbons of Planetary Interest", Icarus, (in press).
- Frenklach, M., Clary, D. W., Gardiner, W. C. and Stein, S. E., "Detailed Kinetic Modeling of Soot Formation in the Shock Tube Pyrolysis of Acetylene", Twentieth Symposium (International) on Combustion, Ann Arbor, MI, 1984, (in press).

- Frenklach, M., Clary, D. W., Yuan, T., Gardiner, W. C. and Stein, S. E., "Shock Tube Pyrolysis of Acetylene: Sensitivity Analysis of the Reaction Mechanism for Soot Formation", *Int. J. Chem. Kinetics* (in press).
- Herron, J. T., Tsang, W., Stein, S. E. and Golden, D., "International Conference on Chemical Kinetics", *J. Phys. Chem.* (in press).
- Hoffbauer, M. A. and Hudgens, J. W., "Multiphoton Ionization Detection of Gas Phase Benzyl Radicals", *J. Phys. Chem.* (in press).
- Huie, R. E. and Neta, P., "Kinetics of One-Electron Transfer Reactions Involving ClO_2 and NO_2 ", *J. Phys. Chem.* (in press).
- Huie, R. E., "Chemical Kinetics of Intermediates in the Antioxidation of SO_2 ", *ACS Symposium Series* (submitted).
- Jackson, W. M. and Okabe, H., "Photodissociation Dynamics of Small Molecules", *Advances in Photochemistry Vol. 13*, Wiley, NY, (in press).
- Karpas, Z. and Lias, S. G., "On the Mechanism of the Reactions of Alkyl Ions with Dialkylhalonium Ions in Alkyl Halides", *J. Org. Mass Spectrom.* (submitted).
- Karpas, Z., Stevens, W. J., Buckley, T. J. and Metz, R., "The Proton Affinity and Gas Phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate and Methyl Thiocyanate", *J. Phys. Chem.* (in press).
- Karpas, Z., "The Proton Affinity of H_2Se , SeCO and H_2CSe and Reactions of Positive Ions with H_2Se ", *Chem. Phys. Letters* (in press).
- Karpas, Z. and Jasien, P. G., "The Proton Affinity Hydro Telluride", *Int. J. Mass Spectrometry and Ion Processes* (in press).
- Kurylo, M. J., Ouellette, P. A. and Laufer, A. H., "Measurements of the Pressure Dependence of the HO_2 Radical Self Disproportionation Reaction 298K", *J. Phys. Chem.* (in press).
- Kurylo, M. J. and Ouellette, P. A., "The Pressure Dependence of the Rate Constant for the Reaction $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$ ($\text{M}=\text{N}_2, \text{O}_2$) at 298K", *J. Phys. Chem.* (in press).
- Lias, S. G., Karpas, Z. and Liebman, J. F., "Halomethylenes: Effects of Halogen Substitution on Absolute Heats of Formation", *J. Am. Chem. Soc.* (in press).
- Manka, M. J., Brown, R. L. and Stein, S. E., "Flow ESR and Static Studies of the Decomposition of Phenyl Substituted Ethanes", *J. Phys. Chem.* (in press).
- Meot-Ner (Mautner), M. and Deakyne, C. A., "The Ionic Hydrogen Bond and Ion Solvation. 5. Predictive Relation for Heats of Hydration. Hydrophobic Solvation of Ions", *J. Am. Chem. Soc.* (submitted).

- Meot-Ner (Mautner), M. and Sieck, L. W., "The Ionic Hydrogen Bond and Ion Solvation. 4. $\text{SH}^+\cdots\text{O}$ and $\text{NH}^+\cdots\text{S}$ Bonds. Correlation with Proton Affinity. Mutual Effects of Weak and Strong Ligands in Mixed Clusters", J. Phys. Chem. 89, 1985 (in press).
- Meot-Ner (Mautner), M., "Conventional and Unconventional Ionic Hydrogen Bonds. Solvation of Protonated Oxygen and Nitrogen Bases", in "Molecular Structure and Energetics", J. F. Liebman and A. Greenberg, ed. (in press).
- Meot-Ner (Mautner), M., Neta, P., Norris, R. K., and Wilson, K., "Temperature Effects on Rates of Dehalogenation of Aromatic Anion Radicals", J. Phys. Chem., 89, 1985 (in press).
- Mautner, M., Rumack, D. T. and Nelson, S. F., "Slow Organic Electron Transfer Reactions", J. Am. Chem. Soc. (submitted).
- Meot-Ner (Mautner), M., Karpas, Z. and Deakyne, C. A., "Ion Chemistry of Cyanides and Isocyanides. 1. The Carbon Lone Pair as Proton Acceptor: Proton Affinities of Isocyanides", J. Am. Chem. Soc. (submitted).
- Meot-Ner (Mautner), M. and Karpas, Z., "Ion Chemistry of Cyanides and Isocyanides. 2. Alkilation of HCN and Cyanides by Oxygen and Sulfur Compounds. Gas-Phase Synthesis and Reactions of Protonated Isocyanides", J. Phys. Chem. (submitted).
- Meot-Ner (Mautner), M., El-Shall, M. S. and Keoterz, M., "Ionic Charge Transfer Complexes. 1. Partially Localized Acceptors and Donors: Dimer Cations of Anilines", J. Am. Chem. Soc. (submitted).
- Neta, P., "Reactions of Radicals with Biologically Important Molecules", in "Chemical Kinetics of Small Organic Radicals", the CRC Press Inc., Boca Raton, FL (in press).
- Neta, P. and Huie, R. E., "Free Radical Chemistry of Sulfite", Environ. Health Persp. (in press).
- Neta, P., Richoux, M. C. and Harriman, A., "One- and Two-Electron Oxidation of Lead (II) Tetrakis (N-Methylpyridyl) Porphyrins in Aqueous Solution", J. Chem. Soc., Faraday Trans. 2, (in press).
- Neta, P., Richoux, M. C., Harriman, A. and Milgrom, L. R., "Resonance Stabilization of Zinc Porphyrin π -Radical Cations", J. Chem. Soc., Faraday Trans. 2, (in press).
- Okabe, H., "Dissociation Energetics of Simple Diazirines by Photon and Electron Impact in the Chemistry of Diazirines M. T. H. Liu, ed., The CRC Press Inc., Boca Raton, FL (in press).
- Richoux, M. C., Neta, P., Harriman, A., Baral, S. and Hambright, P., "One- and Two-Electron Reduction of Metalloporphyrins. Radiation Chemical, Photochemical and Electrochemical Studies. Kinetics of the Decay of π -Radical Anions", J. Chem. Soc., Faraday Trans. 2 (in press).

- Richoux, M. C., Neta, P., Christensen, P. A. and Harriman, A., "Formation and Decay of Zinc Tetrakis (N-Methyl-3-Pyridyl) Porphine - Radical Cation in Water", J. Chem. Soc., Faraday Trans. 2 (in press).
- Robaugh, D. A. and Stein, S. E., "Stabilities of Highly Stabilized Radicals", J. Amer. Chem. Soc. (in press).
- Robaugh, D. A., Tsang, W. and Fahr, A. and Stein, S. E., "Ethylbenzene Pyrolysis C-C or C-H Bond Cleavage, Ber. der Bunsen. Gesell. Phys. Chem., (in press).
- Shaub, W. and Tsang, W., "Hazardous Waste Aspects of Municipal Solid Waste Incinerators", in NBSIR Research in the Characterization of Municipal Solid Waste (in press).
- Sieck, L. W., "Thermochemistry of Solvation of NO_2^- and C_6HNO_2^- by Polar Molecules in the Vapor Phase. Comparison with Cl^- and Variation with Ligand Structure", J. Phys. Chem. (in press).
- Speller, C. V. and Meot-Ner (Mautner), M., "The Ionic Hydrogen Bond and Ion Solvation. 3. Bonds Involving Cyanides. Correlations with Proton Affinities", J. Phys. Chem., 1985 (in press).
- Stein, S. E. and Brown, R. L. "Pathways to Graphite: Properties of Very Large Polybenzoid Hydrocarbons", in "Molecular Structure and Reactivity", Liebman and Greenberg, ed., 1985 (in press).
- Tsang, W. and Hampson, R. F., "Chemical Kinetics Data Base for Combustion Modeling", J. Phys. Chem. Ref. Data (submitted).
- Tsang, W., "Stability of Cyclohexadienyl Radical", J. Phys. Chem. (in press).
- Tsang, W., "Thermal Stability of Perfluoromethyl Bromide", J. Phys. Chem. (in press).
- Tsang, W. and Shaub, W., "Tracers for Quality Assurance in Municipal Solid Waste Incinerator", in NBSIR Research in the Characterization of Municipal Solid Wastes (in press).
- Tsang, W., Walker, J. A. and Kodres, C. A., "The Characterization of Refuse Derived Fuels Using Thermal Methods of Analyses", in Energy from Biomass and Wastes IX (in press).
- Tsang, W. and Robaugh, D. A., "Single Pulse Shock Tube Studies on the Stability of Aromatic Compounds" Proceedings of the 15th Int. Symposium on Shock Waves and Tubes, (in press).
- Walker, J. A. and Tsang, W., "RDF Characterization Using Thermal Method of Analysis", in NBSIR Research on the Characterization of Municipal Solid Waste (in press).

- Brown, R. L., "A Chemical Theory of Graphite", West Virginia University, Morgantown, WV, April, 1985.
- Brown, R. L., "A Chemical Theory of Graphite", Catholic University of America, Washington, D.C., April, 1985.
- Brown, R. L., "A Chemical Theory of Graphite", 17th International Carbon Conference, Lexington, KY, June, 1985.
- Fahr, A., "Rate Constants for Reactions of Phenyl Radicals with Acetylene, Ethylene and Benzene", 17th International Symposium on Free Radicals, Granby, CO, August, 1985.
- Herron, J. T., "Modeling of Complex Chemical Processes: From Planetary Atmospheres to Gaseous Dielectrics", Westinghouse Research and Development Center, Pittsburgh, PA, March, 1985.
- Herron, J. T., "The Thermal Decomposition of S_2F_{10} ", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Herron, J. T., "Chemical Processes Following the Dielectric Breakdown of SF_6 ", Electrosystems Division, NBS, Gaithersburg, MD, August, 1985.
- Hudgens, J. W., "Multiphoton Ionization of Free Radicals", University of Maryland, Chemistry Department, College Park, MD, December, 1984.
- Hudgens, J. W., "Spectroscopy of Free Radicals Using Resonance Enhanced Multiphoton Ionization", ACS meeting, Chicago, IL, September, 1985.
- Hudgens, J. W., "Multiphoton Ionization of Free Radicals", University of Illinois, Chemistry Department, Urbana, IL, September, 1985.
- Hudgens, J. W., "Detection of SF Radicals with Multiphoton Ionization Spectroscopy", 1985 Annual Meeting of the Optical Society, Washington, D.C., October 1985.
- Huie, R. E., "Chemical Kinetics of Intermediates in the Autoxidation of SO_2 ", Symposium on Environmental Effects of Fossil Fuels, 189th Meeting, ACS, Miami, FL, April, 1985
- Huie, R. E., "Kinetics of One-Electron Transfer Reactions Involving ClO_2 and NO_2 in Aqueous Solutions", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Kurylo, M. J., "Recent Laboratory Measurements of SO_x Atmospheric Chemistry: Their Effect on the Atmospheric Modeling Data Base", NASA Panel for Data Evaluation, Washington, D.C., November, 1984.
- Kurylo, M. J., "An Assessment of Laboratory Chemical Kinetic Data for Atmospheric Sulfur Compounds", NASA Panel for Data Evaluation, NOAA, Boulder, CO, February, 1985.

- Kurylo, M. J., "Rate Constant Measurements for HO₂ Reactions of Atmospheric Importance by Kinetic Absorption Spectroscopy", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985
- Kurylo, M. J., "The Pressure Dependence at 298K of the Rate Constants for the Reactions HO₂ + HO₂ and HO₂ + NO₂ + M", XII International Conference on Photochemistry, Sophia University, Tokyo, Japan, August, 1985.
- Lias, S. G., "Reactions of Alkyl Ions with Amines", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Lias, S. G., "Mechanisms of Competitive Condensation - Proton Transfer Reactions", Purdue University, West Lafayette, IN, June, 1985.
- Lias, S. G., "Structures and Reactivities of C₆H₅⁺ Ions", Seventh East Coast Symposium on Ion-Molecular Chemistry, University of Delaware, Newark, DE, October, 1985
- Mautner, M., "Kinetics Controlled Completely by the Reaction Free Energy: Entropy Effects and Fast Endothermic Reactions", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Mautner, M., "Slow Organic Electron Transfer Reactions", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Mautner M., "Free Energy Surfaces with Multiple Wells", Slow Proton Transfer Reactions and Entropy Barriers Due to Steric Hindrance", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June 1985.
- Mautner, M., "The Filling of Solvent Shells About Ions", 10th International Mass Spectrometry Conference, London, England, September, 1985.
- Mautner, M., "Slow Electron Transfer Reactions", 10th International Mass Spectrometry Conference, London, England, September, 1985.
- Neta, P., "Reaction of Peroxyl Radicals with Lipids and Cytochrome P-450: A Study of Model Compounds by Pulse Radiolysis", NIH, Bethesda, MD, December, 1984
- Neta, P., "Redox Reactions of Porphyrins", Miller Conference on Radiation Chemistry, Windermere, England, April, 1985.
- Neta, P., "Redox Reactions of Metalloporphyrins Studied by Pulse Radiolysis. Catalyzed Decay of π -Radical Cations", Ninth DOE Solar Photochemistry Research Conference, New Paltz, NY, June, 1985.
- Neta, P., "Pulse Radiolysis Studies of Porphyrins. Application to Solar Energy Conversion Systems", Pan-American Chemical Congress, San Juan, PR, October 1985.

- Okabe, H., "Photodissociation Dynamics of Simple Molecules-Recent Developments", Chemical Institute of Canada, Queen's University, Kingston, Ontario, Canada, June, 1985.
- Okabe, H., "Recent Development on the Studies of the Photochemistry of Acetylene and Carbondisulfide", Institute for Molecular Science, Okazaki, Japan, August, 1985.
- Okabe, H., "Historical Development of Gas Phase Photochemistry", Mie University, Tsu, Japan, September, 1985.
- Sieck, L. W., "Thermochemistry of Solvation of NO_2^- and $\text{C}_6\text{H}_5\text{NO}_2^-$ by Polar Molecules in the Vapor Phase. Comparison with Cl^- , and Variation with Ligand Structure", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Stein, S. E., "Thermal Chemistry of Polyaromatic Hydrocarbons", Louisiana State University, Department of Chemistry, Baton Rouge, LA, November 1984.
- Stein, S. E., "Kinetic and Thermodynamic Property Estimation Schemes", Fort Detrich, MD, April, 1985.
- Stein, S. E., "Hydrogen Transfer Between Polyaromatic Molecules", International Conference on Chemical Kinetics, NBS, June, 1985.
- Stein, S. E., "Hydrogen Transfer Between Polyaromatic Molecules", ACS Fuel Division Symposium, Chicago, IL, September, 1985.
- Tsang, W., "Single Pulse Shock Tube Experiments on Ignition Behavior", Workshop on Diagnostic of Ignition Mechanisms, Aberdeen, MD, November, 1984.
- Tsang, W., "Unimolecular Processes over Extended Temperature and Pressure Ranges", Technical meeting Eastern Section of the Combustion Institute, Clearwater Beach, FL, December, 1984.
- Tsang, W., "The Characterization of Refuse Derived Fuels Using Thermal Methods of Analysis", IGT Symposium, Orlando, FL, January, 1985.
- Tsang, W., "Energy from Biomass and Wastes IX", IGT Symposium, Orlando, FL, January, 1985.
- Tsang, W., "Chemical Kinetic Data Base for Combustion Modeling", Fort Detrich, MD, April, 1985.
- Tsang, W., "Thermal Stability of Perfluoromethyl Bromide", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.
- Tsang, W., "Mechanism and Rate of Hydrogen Atom Attack in Toluene", International Conference on Chemical Kinetics, NBS, Gaithersburg, MD, June, 1985.

Tsang, W., "CO as a Monitor for Hazardous Waste Destruction Efficiency in MSW Combustion", Office of Municipal Waste Research Panel, Washington, D.C., June, 1985.

Tsang, W., "Single Pulse Shock Tube Studies on the Stability of Aromatic Compounds", 15th Symposium on Shock Waves and Tubes, Berkeley, CA, July, 1985

Tsang, W., "Shock Tube Studies on the Stability of Aromatic Compounds", Department of Chemistry, The Catholic University of America, September, 1985.

7. CHEMICAL KINETICS DIVISION SEMINARS

- Kopplitz, B. D., Princeton University, Department of Chemistry, Princeton, NJ, "Laser-Induced Multiphoton Processes in Aromatic Systems", October, 1984.
- Dean, A. M., Exxon Research and Engineering Company, Annandale, NJ, "Kinetics of Rich CH₄ Flames", November, 1984.
- Klein, D. J., Office of Naval Research, Arlington, VA, "π-Conjugated Polymers: Valence-Bond Description, Solitons, etc.", December, 1984.
- Harriman, A., The Royal Institute, London, England, "Design of Molecular Models for Solar Energy Storage", December, 1984.
- Senthilnathan, V. P., Ohio State University, Department of Chemistry, Columbus OH, "Solid State Chemistry and the Kinetics of Carbenes in Low Temperature Matrices", March, 1985.
- Dalal, N., West Virginia University, Department of Chemistry, Morgantown, WV, "EPR and ENDOR Studies of Pretransitional Cluster Dynamics Near Ferroelectric Phase", March, 1985.
- Greenberg, A., New Jersey Institute of Technology, NJ, "Sources and Fates of Atmospheric Polycyclic Aromatic Hydrocarbons", March, 1985.
- El-Shall, S. S., Georgetown University, Department of Chemistry, Washington, D.C., "Ionic Charge Transfer Complexes: Charge Localized and Delocalized Dimer Ions", April, 1985.
- Laufer, A. H., Department of Energy, Germantown, MD, "Vinylidene: Everything You Wanted to Know (More or Less)", April, 1985.
- Nelsen, S., University of Wisconsin, Department of Chemistry, Madison, WI, "Electron Transfer Reactions with Large Geometry Change", May, 1985.
- Sangster, D. F., CSIRO, Division of Energy Chemistry, Lucas Heights Research Laboratory, Australia, "Radiation Chemistry Research in Australia", June, 1985.
- Bartmess, J. E., University of Tennessee, Department of Chemistry, Knoxville, TN, "Gas Phase Ion Chemistry", July, 1985.
- Dheandhanoo, S., York University, Department of Chemistry, Downview, Ontario, Canada, "Growing Molecules with Ion/Molecule Reactions: Reactions with Diacetylene", September, 1985.
- Kalantar, A. H., University of Alberta, Department of Chemistry, Alberta, Canada, "Extracting First Order Kinetic Results from Noisy Data", October, 1985.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Brown, R. L.

Member, Organizing Committee of Greater Washington Area EPR Discussion Group

Hampson, R. F.

Member, NASA Panel for Data Evaluation

Herron, J. T.

Member, ASTM Subcommittee E47.06 on Environmental Fate of Chemical Substances

Member, ASTM Committee E35 on Pesticides

Chairman, International Conference on Chemical Kinetics, NBS, June, 1985

Huie, R. E.

Member, Environmental Protection Agency Grant Review Panel

Member, Atmospheric Chemistry Working Group, Subcommittee for Atmospheric Research

Kurylo, M. J.

Member, NASA Panel for Data Evaluation

Lias, S. G.

Member, Organizing Committee of NATO ASI on "Structure/ Reactivity and Thermochemistry of Ions", June 29 - July 11, 1986 in Les Arcs, France.

Member, Editorial Board of the series, "Molecular Structure and Energetics", VCH Publishers, Inc.

Member, Editorial Board of the NBS Journal of Research.

Neta, P.

Member, International Commission on Radiation Units and Measurements (Committee on Chemical Dosimetry).

Sieck, L. W.

Lead Panel Member for Small Business Innovative Research Program of the U.S. Department of Energy.

Stein, S. E.

Member, Editorial Advisory Board, International Journal of Chemical Kinetics

Member, Organizing Committee, International Conference on Chemical Kinetics, NBS, June, 1985.

Tsang, W.

Member, Organizing Committee, International Conference on Chemical Kinetics, NBS, June, 1985

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Braun, W., collaborating with A. Laufer of DoE on the design of an improved V.U.V. photolysis - V.U.V. kinetic spectroscopy apparatus.

Brown, R. L., participated in Chemical Research and Development Center Scientific Conference on Observation and Aerosol Research, Aberdeen, Maryland.

Hampson, R. F., participated in the NASA Panel for Data Evaluation meeting, Arlington, VA, 1984.

participated in the NASA Panel for Data Evaluation meeting, Boulder, CO, 1985.

participated in the International Conference on Atmospheric Ozone, Les Diablerets, Switzerland, 1985.

Herron, J. T., collaborated with R. VanBrunt of Electrosystems Division and A. Phelps of JILA on modeling plasma chemistry.

collaborated with J. Sauers, Oak Ridge National Laboratory on chemistry of SF₆ dielectric breakdown.

chaired the International Conference on Chemical Kinetics, NBS, June, 1985.

participated in DoE, Basic Energy Sciences Meeting, Lake Geneva, WI, May, 1985 and acted as secretary for the Informal Panel on Chemical Kinetics.

Huie, R. E., consulted with Raymond E. Hansen, President, Update Instrument, Inc., on the determination of thermal excursions during rapid mixing.

collaborated with C. A. Clarke of South Carolina State University on the ferric-sulfite reaction.

collaborated with S. Jovanovic of CRR on the oxidation of tryptophan and related compounds.

Hudgens, J. W., collaborated with D. Bogan, Catholic University of America on the reactions of F atoms with ketene.

collaborated with C. Dulcey, Naval Research Laboratory on the MPI of free radicals.

Kurylo, M. J., collaborating with A. Fried and R. Sans of the Center for Analytical Chemistry on the detection of HO₂ by dioxide laser spectroscopy.

collaborated with A. H. Laufer of the Department of Energy on the study of the pressure dependence of the gas phase disproportionation of HO₂ radicals.

collaborating with A. H. Laufer of the Department of Energy on the design and fabrication of a laser photolysis ultraviolet absorption apparatus.

provided advisory services to the Upper Atmospheric Chemistry Program of NASA, the Fundamental Interactions Branch of DoE, and the Atmospheric Chemistry Program of NSF.

consulted with A. Kalantar of the University of Alberta on numerical integration techniques for kinetic analysis.

Lias, S. G., Drs. John L. Holmes (University of Ottawa), John E. Bartmess (University of Tennessee), Joel F. Liebman (University of Maryland, Baltimore, County) and David Dixon (Dupont) are collaborating with Sharon G. Lias and Rhoda D. Levin on data evaluation projects for the Ion Kinetics and Energetics Data Center.

Martinez, R. I., provided technical information and consultation regarding the Martinez-Herron Desulfurization Process (U.S. Patent No. 4,351,810) to several international corporations.

consulted with H. Niki, Ford Motor Company on the mechanisms of O_3 -olefin reaction systems and on the photooxidation of formaldehyde.

consulted with P. Dawson, NRC-Ottawa, on CID dynamics of MS/MS tandem mass spectrometers.

consulted with Sam Trevino, U.S. Army, on trajectory calculations and associated kinetics.

consulted with E. K. C. Lee, UC-Irvine, on the mechanism for the matrix photooxidation of H_2CO .

consulted with J. G. Calvert, NCAR, on photooxidation of H_2CO .

consulted with S. Dheandhanoo, York University, on synthetic ion-molecule reactions in SIFT apparatus.

consulted with P. S. Berger, President of Teknivent Corporation, on requisite design and operational characteristics for an MS/MS system controller.

consulted with J. W. Hellgeth, Virginia Polytechnic Institute and State University on FTIR flow-cell interface for HPLC and supercritical fluids.

Mautner, M., collaborated with Dr. C. A. Deakyne, College of the Holy Cross, Worcester, MS on ion clustering energetics.

collaborated with Professor S. Nelsen, Department of Chemistry, University of Wisconsin, Madison, WI on ion chemistry of hydrazines.

collaborated with Professor J. Liebman, Department of Chemistry, University of Maryland, Baltimore on proton affinities of heterocyclic compounds.

Neta, P., collaborated with A. Harriman, Royal Institute, London, England, on kinetics of redox reactions of porphyrins.

collaborated with P. Hambright, Chemistry Department, Howard University, Washington, D.C., on porphyrin reactions.

collaborated with G. Infante, Chemistry Department, Catholic University of Puerto Rico, Ponce, PR, on determination of one-electron reduction potentials of radiosensitizer drugs by pulse radiolysis.

collaborated with L. Pohl, NIH, on destruction of cytochrome P450 by free radicals.

Sieck, L. W., collaborated with the Analytical Mass Spectrometry Group of the Organic Analysis Division, Center for Analytical Chemistry, NBS (White, Christensen) concerning adduct ion formation in MS/MS.

collaborated with R. Van Brunt of the Electrochemical Division, NBS concerning electron transport mechanisms in SF₆.

collaborated with S. Nelsen, Department of Chemistry, University of Wisconsin, Madison, WI, concerning proton affinities of hydrazines.

Stein, S. E., collaborated with A. Greenberg, N. J. Institute of Technology on reactivities of polyaromatic hydrocarbons.

collaborated with M. Frenklach, Louisiana State University on soot formation thermochemistry.

collaborated with W. R. Moore, West Virginia University on synthesis of polynuclear aromatic compounds.

served as reviewer for the R. A. Glenn award for the best paper presented at the fall ACS Meeting Fuel Division Section.

collaborated with K. Kishore, IIS, Bangalore, India, on pyrolysis of polymers.

collaborated with N. Trinastic, Boscovic Institute, Yugoslavia, on theory of graphite.

Tsang, W., collaborated with John Callahan and John Samuels, Edgewood Arsenal, on the interpretation of kinetic data on the decomposition of organic phosphorus compounds.

collaborated with D. Chang, Department of Civil Engineering, U.C., Davis on the interpretation of results from the combustion of hazardous wastes.

collaborated with A. Liftshitz, Hebrew University, Jerusalem on shock tube investigations on the stability of oxygenated hydrocarbons under an Israeli-American binational foundation grant.

served on ONR panel on priority research directions in physical chemistry.

collaborating with G. Mallard, Fire Research, on studies on the stability of aromatic compounds at high temperatures.

10. VISITING SCIENTISTS

- Alfassi, Z., of Ben Gurion University has spent one month at NBS as a guest scientist working on pulse radiolysis.
- Altstein, N., of the Weizman Institute of Science, Israel, is spending two years at NBS as a guest scientist working on pulsed electron sources.
- Chen, R., of West Virginia University has spent six months at NBS as a guest scientist working on free radical chemistry.
- Colussi, A., of University of Mar Del Plata has spent two weeks at NBS as a guest scientist working on high temperature free radical chemistry.
- Fahr, A., has spent one year at NBS under a cooperative agreement with Georgetown University, working on thermolysis of aromatic compounds.
- Fujimoto, G., of University of Maryland has spent six months at NBS as guest scientist working on thermal stability of molecules.
- Griffith, L., of West Virginia University has spent six months at NBS as a guest scientist working on liquid phase pyrolysis studies of aromatic substances.
- Harriman, A., of The Royal Institution, London, has spent three months at NBS as a guest scientist working on pulse radiolysis.
- He, Yu Zhong, of the Institute of Mechanics Academia Sinica, Beijing, has spent six months at NBS as a guest scientist working on shock tube studies on thermal stability of molecules.
- Hoffbauer, M., of West Virginia University has spent six months at NBS as a guest scientist working on chemical processes in molecular beams using laser techniques.
- Kafafi, S., of the University of Cairo has spent six months at NBS as a guest scientist working on polynuclear aromatic hydrocarbons.
- Karpas, Z., of the Nuclear Research Center, Negev, Israel, spent a year at NBS as a guest scientist working on the kinetics of ion-molecular reactions using the ion resonance spectrometer.
- Laufer, A., of the Department of Energy has spent one day a week at NBS working on free radical species.
- Manka, M., of Catholic University has spent six months at NBS as a guest scientist working on thermolysis of organic compounds.
- Mosseri, S., of Ben Gurion University of the Negev has spent six months at NBS as a guest scientist working on pulse radiolysis.
- Richoux, M.-C., of The Royal Institution, London, has spent one year at NBS as a guest scientist working on pulse radiolysis experiments.

Robaugh, D., of West Virginia University has spent ten months at NBS as a guest worker working on high temperature shock tube studies of aromatic pyrolysis.

Rumack, D., of the University of Wisconsin has spent two months at NBS as a guest scientist working on mass spectrometry of hydrazine derivatives.

Senthilnathan, V., of West Virginia University has spent seven months at NBS as a guest scientist working on free radical reactions on high temperature fluids.

Speller, C., of the University of Paris completed a year at NBS as a guest scientist working on ion chemistry.

Walker, J., of West Virginia University has spent one year at NBS as a guest scientist working on thermal stability of organic compounds.

CHEMICAL THERMODYNAMICS DIVISION

Stanley Abramowitz, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

1. INTRODUCTION

A. Objectives

Chemical Thermodynamics provides measurement techniques, concepts and data on the energetics and equilibria of chemical processes. Among the uses of chemical thermodynamics are the prediction of equilibria in chemical reactions, thermodynamic properties of high temperature refractory materials and gases, activities of aqueous solutions used in such diverse technologies as power generation, biotechnology and electrorefining. This Division develops the models necessary for correlating structure with thermodynamic properties, develops the science of calorimetry in order to obtain precise data from the microjoule to megajoule levels, carries out precise thermodynamic measurements, including those on Standard Reference Materials, develops the measurement capabilities for molecular structure determinations and critically evaluates thermodynamic data in all phases for the use of industry, government and academia. A particular emphasis is being directed towards biothermodynamics and biomolecular structure which will yield basic data, measurement techniques standards and concepts for the emerging biotechnology industry.

Specific objectives of the Chemical Thermodynamics Division include:

- o Application of the science of calorimetry to the needs of existing and new technologies through the design of novel calorimeters and the development of improved procedures to attain enhanced measurement precisions and accuracies.
- o Development and certification of Standard Reference Materials.
- o Measurement of thermodynamic properties of key chemical species and processes including phase transitions of biomolecular species.
- o Development of measurement techniques to characterize the molecular structure of biopolymers such as proteins and DNA using the techniques of x-ray and neutron diffraction in order to establish structure function relationships.
- o Provision of critically evaluated compilations on the chemical thermodynamic properties of inorganic and organic compounds.

- o Development of estimation methods for the prediction of thermodynamic properties of organic and inorganic species in the gaseous, liquid, solid and aqueous phases.
- o Response to the needs of industry, government and academia for thermodynamic and related information.

B. Organization and Staff

The Chemical Thermodynamics Division is organized into three major groups. These groups are:

- o Biothermodynamics and Molecular Structure, S. Abramowitz, Group Leader
- o Chemical Thermodynamics Measurements, E. S. Domalski, Group Leader
- o Chemical Thermodynamic Data Centers, D. Garvin, Director, Chemical Thermodynamics Data Center

The division has 22 full-time staff, 3 part time employees, 4 guest workers, 4 students, 6 contractors, 1 IPA and 1 consultant. This past year we have added two new research areas one in Biomolecular Structure, using the techniques of x-ray and neutron diffraction and one in Differential Scanning Calorimetry of Biopolymers. A librarian - information specialist has been added to the Chemical Thermodynamics Data Center. Several guest workers have joined the staff.

We regret to have to report the death, in June 1985, of William H. Evans. Dr. Evans, a coauthor of NBS Circular 500 and the "NBS Tables of Chemical Thermodynamic Properties" retired in 1977 but remained a very active participant in the work of the data center until his death. The master index to thermodynamic measurements, in design and operation, and the present form of the Bulletin of Chemical Thermodynamics are monuments to his skill and perseverance.

C. Research for NBS Programs

The division participates in the work of two of the NBS programs.

Office of Standard Reference Data

- o Evaluation of thermochemical properties of inorganic species.
- o Development of a data base management system for chemical thermodynamics.
- o Development of critically evaluated data and reliable estimation schemes for organic and biochemical species.

Office of Standard Reference Materials

- o Certification of heating value, residual moisture, ash and sulfur content of coals, SRM 2682, 2683, 2684, 2685.
- o Certification of synthetic refuse-derived fuel, SRM 1657.
- o Certification of an oxygen bomb calorimetry standard reference materials, thianthrene, (SRM 1656); nicotinic acid, (SRM 2151); and urea (SRM 2152).
- o Research to develop a phosphorous containing organic compound for an oxygen bomb calorimetry standard.

D. Other Agency Research

The research needs of two federal agencies and one industrial trade association are being addressed by the Division. The funding agency, NBS manager/investigator, and programs are given below.

<u>Funding Agency</u>	<u>NBS Program Manager/ Investigator</u>	<u>Program Title/ Description</u>
Department of Defense Air Force Office of Scientific Research (AFOSR)	S. Abramowitz D. A. Ditmars	High temperature thermo- dynamic measurements on ceramics, pure elements and compounds
Department of Energy Pittsburgh Energy Technology Center (PETC)	D. Garvin R. N. Goldberg V. B. Parker D. Smith-Magowan	Thermodynamic data for flue gas clean-up in fossil fuel technology
Department of Energy Energy from Municipal Waste (EMW)	E. S. Domalski K. L. Churney A. E. Ledford S. S. Bruce T. J. Buckley	Chlorine content of municipal solid waste; Threshold condition for the formation/destruct- ion of chlorinated organic species.
Design Institute for Physical Property Data (DIPPR)	D. Garvin R. N. Goldberg T. L. Jobe, Jr. D. Smith-Magowan	Bibliographies of thermodynamic data on sour water and various salt systems.
U.S. Department of the Army, Aberdeen Proving Ground	E. S. Domalski D. R. Kirklin	Combustion calorimetry and estimation methods for organic phosphorus compounds.

Solar Energy Research
Institute (SERI)

E. S. Domalski
T. L. Jobe, Jr.

Revision and up-date of
previous publication on
thermodynamic data for
waste incineration.

E. Collaborations within NBS

In addition to the interactions with other NBS programs and federal agencies, the Division collaborates with other NBS units. Among these are:

With CCP

- joint program with Chemical Kinetics Division on Database Management Systems
- collaboration with Chemical Kinetics and Molecular Spectroscopy Division on carrying out and planning a research program in support of the high temperature technology needs of AFOSR.
- collaboration with Surface Science Division in developing algorithms for the interpretation of sputtering depth profiles

With NML

- cooperation with Center for Analytical Chemistry in planning a program initiative for Biotechnology.
- cooperation with Center for Analytical Chemistry in determining trace organic chlorine constituents in combustion products
- cooperation with OSRM and OSRD in planning standards reference materials and evaluated data needs
- cooperation with Center for Basic Standards on temperature measurements in combustion studies

With IMSE

- collaboration in planning and carrying out a research program in support of AFOSR needs in high temperature technologies

With NEL

- collaboration in planning and carrying out a research program in support of AFOSR high temperature technology needs

Our staff has many interactions with voluntary standards organizations and international societies such as ASTM, ANSI, ASME, CODATA, IUPAC, IAEA etc. Staff members hold memberships on diverse committees ranging from environmental and health concerns to energy utilization to data base management.

The breadth of scientific interest is shown in the discussions of current projects in the body of this report. While these reports show the scientific content of the Division's work, they do not show individual scientific achievements, participation of the staff in NBS programs, extensive interactions with other federal agencies, standards organizations and international scientific organizations. Some of the individual achievements of particular note are given below.

Eugene Domalski gave an invited talk at the 5th International Symposium on Chlorinated Dioxins and Related Compounds at University of Bayreuth, Bayreuth, West Germany.

David Garvin gave an invited talk on Recent Evaluations of Thermochemical Properties of C₁-C₆ paraffins at a Symposium on Natural Gas Measurements at the Institute for Gas Technology, Chicago, Ill.

Alex Wlodawer authored a chapter in Neutrons in Biology entitled "Application of Joint Neutron and X-ray Refinement of the Structure of Ribonuclease A at 2Å Resolution".

William H. Kirchhoff authored a report entitled "A National Program of Measurement Services and Standards for Biotechnology at the National Bureau of Standards" for the U.S. Congress.

In FY 85 our program has become less involved in applied programs. We have been successful in raising funds for more research in biothermodynamics and biomolecular structure. In particular a laboratory for molecular structure is being outfitted. A staff member, Alex Wlodawer, has joined the division together with three guest workers and a NRC postdoctoral fellow. This group is using the techniques of x-ray and neutron diffraction to obtain structures of proteins, enzymes and DNA species. A Hart differential scanning calorimeter which has been designed for biological standards has been installed in a new laboratory. Fred Schwarz has joined the division and is pursuing a research program using this instrument. He is collaborating with researchers from NIH and FDA.

In FY86 we will continue our efforts in the biothermodynamics and biomolecular structure area. Work will continue in the thermodynamics and enzyme catalyzed reaction, differential scanning calorimetry of proteins and other biopolymers, molecular structure determinations of biopolymers including enzymes, proteins and DNA fragments, critical data evaluation and development of predictive schemes for organic and biomolecular species.

Work will also continue on the determination of enthalpies of formation of key phosphorous compounds and biomolecular building blocks. This will be done in a symbiotic manner with cooperation between data and predictive programs in order to produce reliable predictive schemes. Benzoic acid will be recertified. Research to characterize the effluents resulting from the combustion of municipal solid waste will be continued.

Plans for the data activities include an expansion into the area of thermal functions with an addition to the staff. The additional staff member, Malcolm Chase of the Dow Chemical Corporation, will afford us a direct link between the high temperature experimental programs in CCP, CCE and IMSE and data evaluation. Work will continue on CODATA and key values projects.

2. BIOTHERMODYNAMICS AND MOLECULAR STRUCTURE

S. Abramowitz, E. Gajewski, R. N. Goldberg, R. W. Harrison
W. H. Kirchhoff, M. Miller, H. Savage, F. P. Schwarz, D. Steckler,
Y. B. Tewari, I. Weber, A. Wlodawer

A. Thermodynamics of Enzyme Catalyzed Reactions (E. Gajewski, R. N. Goldberg, D. Steckler and Y. B. Tewari)

Accurate thermodynamic data on biochemical reactions are needed to facilitate a better understanding of the reactions themselves and for the optimization of product yields for reactions having industrial significance. The goal of this effort is to provide reliable thermodynamic data (equilibrium constants, enthalpies, and heat capacities) for biochemically and industrially important reactions and the associated measurement and computational techniques. The accomplishments of this past year are in several areas: (1) measurements on specific enzyme-catalyzed reactions, (2) development of chromatographic separation techniques, (3) studies of the feasibility of isomerization reactions of carbohydrates which are catalyzed by glucose isomerase, (4) additions to and refinement of the software used for running calorimetric experiments, and (5) applications of computational procedures to the treatment of data involving complex equilibria. The focus of the research has been on item (1) above with the other items (2-4) being necessary for its proper accomplishment.

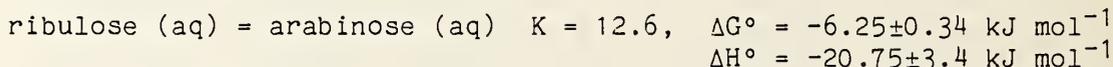
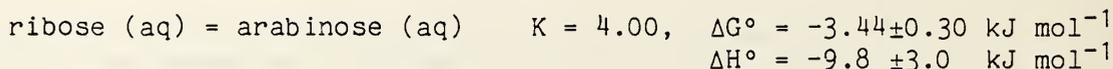
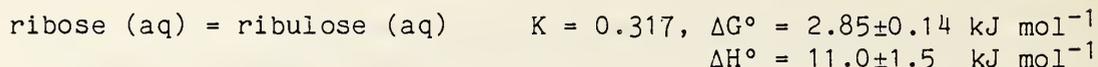
The specific enzyme-catalyzed reactions which have been investigated are: (1) The conversion of xylose to xylulose, (2) ribose to ribulose and to arabinose, (3) aspartic acid to fumaric acid and ammonia, and (4) the hydrolysis of adenosine 5'-triphosphate (ATP) to adenosine 5'-diphosphate (ADP) and inorganic phosphate. Summaries of the results of these investigations follow.

(a) xylose(aq) = xylulose(aq)

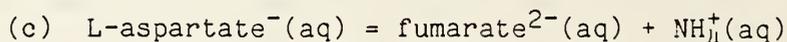
This reaction, an intermediate step in the conversion of biomass (hemicellulose) to ethanol, was carried out in aqueous phosphate buffer over the pH range 6.8 to 7.4 using solubilized glucose isomerase with MgSO_4 as a cofactor. The temperature range over which this reaction was investigated was 298.15 to 342.15 K. A combined analysis of both the HPLC and microcalorimetric data leads to the following results at 298.15 K for the conversion process: $K = 0.170$, $\Delta G^\circ = 4.39 \pm 0.03 \text{ kJ mol}^{-1}$, $\Delta H^\circ = 16.09 \pm 0.67 \text{ kJ mol}^{-1}$, and $\Delta C_p^\circ = 40 \pm 23 \text{ J mol}^{-1} \text{ K}^{-1}$.



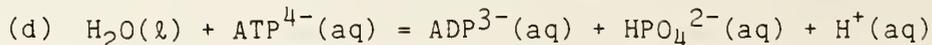
These reactions were carried out in aqueous phosphate buffer over the pH range 6.8 to 7.4 and over the temperature range 313.15 to 343.75K using solubilized glucose isomerase with $Mg(NO_3)_2$ and $MgSO_4$ as cofactors. The equilibrium constants and the standard state Gibbs energy and enthalpy changes at 298.15 for these equilibria are:



Qualitative information on the rates of the above reactions was also obtained. The existence of arabinose as an isomerization product had not been previously reported in the literature.



The above reaction which is catalyzed by aspartase, was carried out in aqueous phosphate buffer over the pH range 7.25 to 7.43, the temperature range 268.15 to 316.15K, and at ionic strengths varying from 0.066 to -0.366 mol kg⁻¹. The treatment of the experimental data requires detailed modelling calculations involving not only all of the species involved in the above process, but also the species formed from malate. Effects of ionic strength on the activities of all of the species were included in all the equilibrium calculations. The following values were found for the above process at 298.15K and at zero ionic strength: $K = (1.48 \pm 0.08) \times 10^{-3}$, $\Delta G^\circ = 16.15 \pm 0.13 \text{ kJ mol}^{-1}$, $\Delta H^\circ = 24.5 \pm 1.0 \text{ kJ mol}^{-1}$, and $\Delta C_p^\circ = -147 \pm 100 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculations have also been performed which give values of the apparent equilibrium constant, $(\Sigma \text{ fumarate}) (\Sigma \text{ ammonia}) / (\Sigma \text{ L-aspartate})$, as a function of temperature, pH, and ionic strength. The above value for ΔG° , when adjusted to an ionic strength of 0.1 mol kg⁻¹, fits well into a thermochemical cycle calculation recently performed by D. Smith Magowan of the Electrolyte Data Center. The industrial synthesis of L-aspartic acid uses the above process.



This reaction is currently the subject of a calorimetric investigation where the effects of variations of pH, temperature, and ionic strength on the molar enthalpy of reaction are being determined. The buffer selected was TRIS/HCl. Thus far, the pH has been varied from 6.4 to 8.8 and the ionic strength from ~ 0.1 to ~ 0.6 mol kg⁻¹. It has been found that the enthalpy of reaction is a constant over the pH range 8.3 to 8.8 in agreement with the predictions of equilibrium calculations,

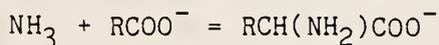
but that the enthalpy varies by 2.7 kJ mol^{-1} due to a change of ionic strength of $\approx 0.5 \text{ mol kg}^{-1}$. At a pH of 8.5 and an ionic strength of 0.1 mol kg^{-1} , the tentative value of ΔH_D is $20.5 \pm 0.2 \text{ kJ mol}^{-1}$. The understanding of the energetics of this process is of particular significance due to the ubiquitous nature of ATP in biochemical processes.

Three of the above investigations used HPLC for the quantitative separation and analysis of the equilibrium reaction mixtures. The ATP study also used HPLC to establish the purity of the ATP and to confirm the absence of side reactions. The chromatographic separations were performed using calcium cation exchange columns. Quantitative separations have also been obtained for glucose 6-phosphate, fructose 6-phosphate, glucose, and fructose using a quaternary-ammonium ion-exchange column. These separations will allow thermodynamic investigations involving the phosphorylation of glucose and fructose as well as for the isomerization of glucose 6-phosphate to fructose 6-phosphate.

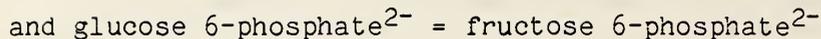
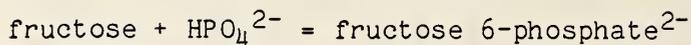
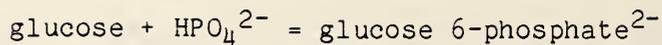
Preliminary investigations have also been performed on the isomerization of the hexoses, allose, altrose, galactose, talose, psicose, sorbose, and tagatose. It has been found that an equilibrium was established between aqueous allose, altrose, and psicose after one week in the presence of glucose isomerase at 60°C . This reaction has not been previously reported in the literature. If feasible, a detailed equilibrium investigation may be undertaken. The other hexoses showed no detectable isomerizations under similar conditions.

High precision microcalorimetry was used in the above investigation for the direct measurement of the enthalpy changes of the enzyme-catalyzed reactions (a-d). This past year the software used for the conduct of the experiments and for the calculation of results from the experiments has been improved. At present, three microcalorimetric experiments can be conducted simultaneously with automatic data requisition and convenient calculation of results. An algorithm has also been developed for the deconvolution of the experimental thermograms to yield a thermo-kinetic curve of the process which has occurred in the microcalorimeter.

Plans for the coming year include completion of the ATP hydrolysis study, documentation of the microcalorimetric procedures and the computer software used for data acquisition and calculation and, if possible a study of the equilibrium between allose, altrose and psicose. Trans aminase reactions of the type



will be studied which are relevant to the industrial synthesis of amino acids such as phenylalanine and tyrosine. The chromatographic separations obtained using the quaternary ammonium columns enable the study of the following fundamental phosphorylation and isomerization reactions:



B. Differential Scanning Calorimetry (F. P. Schwarz and W. H. Kirchhoff)

Differential scanning calorimetry provides information on the thermodynamics of conformational changes occurring in proteins, nucleic acids and polysaccharides and of phase changes occurring in lipids and biological membranes. This information is useful in characterizing the interactions between components of biological systems, such as the chemical binding between an enzyme and substrate, the structural properties of biological molecules and the thermal stability of proteins in solution. There is also a need for temperature and transition enthalpy standards based on biological systems to calibrate the heat capacity and temperature measurements of a differential scanning calorimeter in the temperature range from 0 to 100°C.

1. Temperature and Enthalpy Standards for Differential Scanning Calorimetry (F. P. Schwarz)

The di-alkylphosphatidylcholines are a class of lipids which undergo sharp phase transitions in aqueous solutions below 100°C. These species have been proposed as standard reference materials for the calibration of DSCs. The di-alkylphosphatidylcholines consist of two long hydrophobic alkyl chains and a hydrophilic aminoalkylphosphate head group. When suspended in water these species form bilayers with the polar head group on the exterior of the bilayer. The bilayers undergo a gel to liquid crystal phase change in which the alkyl chains change from an all trans configuration to a mixture of trans and gauche configurations (main transition) and a smaller, bilayer surface configurational change at a lower temperature (pre-transition). Specifically, the enthalpies of the main transitions are on the order of 5-10 kcal/mole and occur at temperatures from 12.6°C (1,2-dielaidoyl-L-phosphatidylcholine) to 65.5°C (1,2-diarachidoyl-L-phosphatidylcholine).

Suspensions of the phosphatidylcholines in pH=7.0 buffered aqueous solutions were prepared and stored under a variety of experimental conditions similar to those found in biological laboratories. It was observed that the main and pre-transition enthalpies depended on the preparation and storage conditions of the suspensions and that under certain storage conditions additional transitions were observed at lower temperatures. A phase transition, corresponding to a change in the alkyl chain packing from orthorhombic to quasihexagonal, was observed at 8°C for 1,2-dimyristoyl-L-phosphatidylcholine. This transition only had been previously observed for 1, 2 dipalmitoyl-L-phosphatidylcholine and 1,2 distearoyl-L-phosphatidylcholine. Despite the variation of the transition

enthalpies, in some samples on the order of 20%, the temperature of the main phase transition remained within 0.05 centigrade degrees for all the phosphatidylcholines studied. For this class of lipids suspended in buffered water solutions, the temperature of the main phase transition could serve as a temperature standard for calibrating the temperature measurements of DSCs. They would however not be useful for enthalpy standards.

Ribonuclease a and Lysozyme exhibit unfolding transitions in the temperature range of 20°C to 80°C which could be used as enthalpy standards for the calibration of the transition enthalpy measurements of the DSC. The enthalpies and temperatures of the unfolding transitions of these proteins were measured as a function of pH to evaluate their potential as enthalpy standards. Preliminary results indicate that the transitions are not fully reversible because of some thermal degradation above the transition temperature and that the transition enthalpies are dependent on pH. For example the enthalpy of Ribonuclease a increases by 30% in going from a pH 3.0 to a pH 4.0 buffer solution. The results however, are reproducible and are not dependent upon storage conditions.

2. The Thermal Stability of Clathrin Structures (F. P. Schwarz and W. H. Kirchhoff in collaboration with C. Steer and I. W. Levin of NIH)

The coated vesicles in eukaryotic cells have been implicated in a variety of shuttling processes within the cell such as the transfer of proteins and lipids from the cell membrane to the interior of the cell. The coated vesicles consist of lipid vesicles enclosed in a polyhedral protein lattice consisting basically, of trimers of 180-kDal clathrin molecules in association with smaller 35-kDal polypeptide units. Under mild alkaline conditions (pH=8.5) the lattice coating is dissociated from the coated vesicle and breaks down into units termed triskelions which consist of the clathrin trimers associated with the smaller polypeptide units. In weakly acidic solutions (pH=6.5), the triskelions reassemble into cage-like structures with lattices similar to those of the coated vesicles. From 15 to 95°C, buffer solutions of the coated vesicles exhibit one transition at $55.7 \pm 0.1^\circ\text{C}$ with an enthalpy of transition of $10.5 \pm 0.2 \text{ j/g}$ and a van't Hoff enthalpy of $1.79 \pm 0.01 \times 10^6 \text{ j/mole}$. The cooperativity of the transition, determined from the ratio of the enthalpy to the van't Hoff enthalpy (using a molecular weight of 540-kDal for the clathrin trimer unit), is 3.17 ± 0.06 indicating that three cooperative regions are participating in the transition. Solutions of the reassembled cages exhibit two transitions over the same temperature range: at $53.0 \pm 0.2^\circ\text{C}$ with a transition enthalpy of $4.6 \pm 0.3 \text{ j/g}$ and a van't Hoff enthalpy of $1.20 \pm 0.01 \times 10^6 \text{ j/mole}$ and at $56.1 \pm 0.1^\circ\text{C}$ with transition enthalpy of $3.7 \pm 0.1 \text{ j/g}$ and a van't Hoff enthalpy of $2.81 \pm 0.09 \times 10^6 \text{ j/mole}$. The cooperativities are 2.1 ± 0.1 for the lower temperature transition and 0.71 ± 0.02 for the higher temperature one. In contrast, solutions of the triskelions exhibit no transitions over the same temperature range. Infrared spectroscopic studies show that the alpha helix structure of the triskelions decreases substantially as they

reassemble into cages and that the structural properties of the triskelions in the reassembled cages are very similar to the structural properties of the triskelions of the coated vesicles. The decrease in the alpha helix structure would reduce the thermal stability of the triskelion as is observed in the DCS results.

3. The Thermal Stability of Serum Albumin (F. D. Schwarz in collaboration with A. Shrake of the FDA)

Serum albumin is the most abundant protein in human plasma, accounting for 60% of the normal concentration of 42g/l, and it functions as a transport protein in the blood. Commercial processing of 5% normal serum albumin solution requires heating the solution at 60°C for 10-11 hr. Since this temperature is close to the thermal denaturation temperature of 66.8°C, for undefatted serum albumin, small concentrations of N-acetyltryptophanate and octanoate are added to the solution to increase the thermal stability of the albumin by complexing with the albumin. For example, a combination of 4mM N-acetyl-DL-tryptophanate and 4 mM octanoate increases the denaturation temperature to 75.9°C. The tryptophanate, however, can induce photodegradation of the solution since it absorbs room light. In a previous study, it was observed that 4 mM octanoate alone increases the thermal stability of the serum albumin to a denaturation temperature of 75.3°C and that the presence of the thermal stabilizers at subsaturated concentrations induces a second transition at a higher temperature (bimodality).

To elucidate the bimodal nature of the denaturation transition and to identify other thermal stabilizers not susceptible to photodegradation, a study was initiated to determine the effect of different concentrations of octanoate and other fatty acid anions on the thermal stability of serum albumin. To date, the thermal stability of solutions of human defatted serum albumin containing concentrations of butanoate, hexanoate, heptanoate, octanoate, and decanoate anions has been determined from 30°C to 100°C. For all the solutions studied, the denaturation temperature increases to a maximum value as the anion concentration is increased and then levels off with a very slight decrease at very high anion concentration. This increase is also accompanied by an increase in the enthalpy of transition to a constant value at high concentrations. The maximum thermal stability is achieved with 73 mM octanoate where the denaturation occurs at 87.3°C. The transition bimodality begins to appear with the octanoate anions and becomes more pronounced with increase in the anion chain length which also increases the binding affinity between the anion and the serum albumin. A model has been proposed based on ascribing the bimodality to the presence of two protein species in the solution and to migration of the anion ligands from the more labile species to the more stable species as the former unfolds; such migration would increase the stability of the latter. The model has been successful in predicting the extent of migration from the magnitudes of the affinity of the albumin for ligand and from the magnitude of the maximum increase in thermal stability (the magnitude of the temperature shift). This model

is important since the bimodal thermograms exhibited by proteins in the presence of a substrate in solution may be explained by ligand migration and not be related to the macromolecular substructure of the protein.

In FY 86 the unfolding transitions of proteins in solution will be investigated in more detail with regard to their applicability as enthalpy standards for DSC measurements. The relationship between the enthalpy and temperature of the transition will be investigated for model systems. The dependence of both of these parameters on pH will also be determined. The serum albumin thermal stability study will be extended from fatty acid chain lengths of 10 carbons to 18 carbons where the bimodality is more pronounced. The thermal stability of novel DNA oligonucleotides in solution will also be investigated to determine their equilibrium configurations in solution.

C. Spectroscopic Characterization of Phase Transitions in Biomolecules (W. H. Kirchhoff)

The two-state model for phase transitions in biomolecules which was developed for Raman Spectroscopy studies of lipid bilayers has been shown to be generally applicable to other spectroscopies and to other biomolecular systems. The model derives from the thermodynamic properties of small systems as described by Hill.

The statistical analysis of phase transition data has been made more robust through a novel means of dealing with a paucity of data in the phase transition region. The analytical expression for the two state model as it applies to spectroscopic data is given in its simplest form by

$$I = \frac{A}{1+e^t} + \frac{B}{He^{-t}} \quad (1)$$

where t is the scaled temperature, $t = (T-T_0)/D$. T_0 is the midpoint of the transition and D is the width parameter for the transition region. The parameters T_0 and D are determined by the data falling in the phase transition region. A statistical method has been developed to estimate the width of the transition interval which is based on the precision of the data in the asymptotic limits. The number of data points falling within this estimate of the transition interval determines the confidence interval within which T_0 and D can be estimated. Even in situations where only one or no data fall within the interval, upper bounds can be placed on the value of D . The program has been extensively documented and is available for distribution.

The function in equation (1) is known as the logistic function and has the differential form $dy/dx = y(1-y)$. In the differential form, the logistic function strongly resembles the Gaussian function but with longer tails. It has been extensively used in statistics because of this resemblance and because of its greater analytical simplicity in its cumulative form. The cumulative form, equation 1, is widely encountered in

chemistry (autocatalysis, bimolecular reactions, oxidation-reduction potentials) and the statistical analysis program, with minor modification, should be applicable to these classes of data as well.

During the next fiscal year, three projects will be undertaken. The logistic function analysis program will be applied to sputter depth profiles as a systematic procedure for parameterizing the interface between dissimilar materials. The analysis will be used in the certification of standard reference materials being developed in the Surface Science Division for the characterization of metal interfaces. The two state model for phase transitions in small systems will be extended to the numerical analysis of differential scanning calorimetric measurements with the objective of developing a standardized method of data reduction and parameter estimation. Finally, an existing molecular dynamics code (CHARMM or AMBER) will be adapted to run on the new NBS Cyber 205 computer and will be evaluated for its usefulness to division programs in biotechnology.

D. Biomolecular Structure Studies

(A. Wlodawer, R. Harrison, M. Miller, H. Savage, I. Weber)

Introduction

The aim of the Macromolecular Structure Group is to develop an active program of measurement and analysis of the structures of biologically important macromolecules. The molecules under study include proteins, enzymes, enzyme inhibitors, hormones, DNA and also assemblies of molecules such as proteins complexed with DNA. The biological activity depends on the structure and dynamics of these macromolecules which are of general interest in the field of biotechnology. For example, the structure of an enzyme may be altered by the binding of an inhibitor molecule so that the structure in the presence and absence of the specific inhibitor may be necessary to understand the function. Enzymatic function may also be elucidated by analyzing the structure of several mutant proteins.

The principal experimental techniques used by the group are X-ray and neutron diffraction from single crystals and neutron small angle scattering from solution. We also rely on collaborations with other scientists who analyze the biological functions of these molecules in vivo and in vitro. The determination of a macromolecular structure passes through three major stages. First, single crystals must be grown; then the structure must be solved by X-ray diffraction; and finally the structure must be refined at high resolution, including neutron diffraction data if possible, in order to produce a highly accurate model with all hydrogen atoms and the surrounding solvent molecules. The experimental program proceeds through crystallization studies to X-ray and neutron diffraction measurements. Then the structure must be built and analyzed by computer graphics system and at that stage extensive computations are required. The simultaneous determination of biomolecular structures using both X-ray and neutron diffraction data is unique to the NBS program. Neutron data,

unlike X-ray data, allow accurate placement of hydrogen atoms. The experimental program is augmented by the development of better tools for each experimental stage. We are developing better computer techniques for solving macromolecular structures, for analyzing and modeling structures, and for understanding the dynamics of biological systems.

The projects described below vary in their objectives from attempts to describe the modes of interaction of proteins and nucleic acids at very low resolution, to solving the structures of several proteins at near-atomic resolution and refining structural models at very high resolution including hydrogen atoms and water molecules. Several different biological systems are under investigation including proteins that activate genes; enzymes that have chemotherapeutic activities and a sweet tasting protein. We are also interested in the interactions between macromolecules and solvent since almost all biologically important reactions take place in aqueous media.

1. Structural Studies of Three Antitumor Amidohydrolases
(I. Weber, A. Wlodawer and R. Harrison)

Three bacterial amidohydrolases with antitumor properties have been crystallized: a glutaminase-asparaginase (Gase) from Acinetobacter glutaminasificans, a Pseudomonas 7A Gase and a Vibrio Succinogenes asparaginase (Ase).

The enzymes are tetramers with subunit molecular weights of ca. 34,000 daltons. The Acinetobacter Gase crystallizes in space group I222 with one subunit per asymmetric unit. Native data are available to 2.9Å; MIR data (3 derivatives, 4.7-4Å) permitted the direct phasing of 2617 reflections. Extension of the phases for an additional 4784 reflections (2.9Å) and phase improvement was achieved with two complementary density modification techniques.

These were (a) the method of B. C. Wang that flattens the solvent region and improves protein connectivity and (b) the method devised by R. W. Harrison that maps the distribution of density values onto a Gaussian distribution with the same mean and standard deviation. It proved possible to fit a polyalanine chain to the density, although the connectivity is ambiguous in several places.

The map produced by R. W. Harrison allowed the tracing of a polypeptide chain into parts of the solvent that were masked in the map computed with the algorithm of B. C. Wang. These coordinates yielded an initial R of .48; R = .34 following refinement. In the absence of a known amino acid sequence, the amino acid types have been estimated resulting in an improved fit of the model to the electron density. The R factor for the coordinates with a guessed sequence is now .30. The polypeptide chain folds into two domains. The amino terminal domain consists of a five-stranded β -sheet and four α -helices. The second domain is less well determined.

6A intensity data are presently available for a form of the homologous Pseudomonas GAase with one tetramer per asymmetric unit; space group $P2_12_12_1$. The structure was initially solved with rotation and translation function techniques, using a 3.2Å Acinetobacter GAase map as a starting point. The Acinetobacter GAase polyalanine coordinates confirmed the solution. The 3.2Å map also has been used to solve the rotational problem for the Vibrio Ase. This protein crystallizes in space group $P22_12_1$ with a dimer in the asymmetric unit.

2. Structural Studies of Mutations in Catabolite Gene Activator Protein
(I. Weber)

Catabolite gene activator protein (CAP) regulates transcription of genes in *E. coli*. In the presence of allosteric activator, cyclic AMP, (CAMP). CAP binds to specific DNA sequences at several operons, causing the stimulation or repression of transcription. The crystal structure of a dimer of CAP with bound CAMP was solved (McKay and Steitz) at Yale University.

CAP with an altered amino acid sequence is being investigated by Dr. Alan Peterkofsky at NIH. Three CAP mutants, crp 91, crp 220 and crp 222, that function in the absence of CAMP, have been sequenced. The amino acid changes are: Ala 141 to Thr in crp 91; Thr 127 to Ile and Gln 170 to Lys in Crp 220; and Thr 127 to Ile, Gln 170 to Lys and Leu 195 to Arg in crp 222. Crystallization trials have been performed on these three mutants in order to study the relation of structure to functional changes. Crp 91 forms crystals with CAMP under the same conditions as wild type CAP. Both crp 91 and crp 222 form crystals with CAMP under different conditions using polyethylene glycol as precipitant. These 3 crystal forms have similar unit cell dimensions to the crystals of wild type CAP, so it should be relatively easy to solve the structures of the mutant proteins.

3. Predicted Structure for Two Domains of the Regulatory Subunit of CAMP-dependent Protein Kinase
(I. Weber)

The mammalian CAMP dependent protein kinase regulates various biochemical reactions by phosphorylating enzymes in the presence of CAMP. The activator, CAMP, is bound in the regulatory subunit. The structure of the regulatory subunit is not known, however it can be predicted by analogy with the known structure of catabolite gene activator protein (CAP). CAP and protein kinase are both activated by CAMP. The amino acid sequences have been determined of the regulatory subunits type I and II, (RI) and (RII). Both sequences are homologous to each other and to the sequence of catabolite gene activator protein from *E. coli*. Therefore, the structure of CAP has been used as a model for the unknown structures of the two homologous domains of RI and RII. The sequences of RI and RII have been fitted to the CAP structure using a computer graphics system. The model structures have similar binding sites for CAMP. The validity of

the model structure will be tested by comparing the predicted CAMP-protein interactions with those deduced from experimental studies of the binding of CAMP analogs to RI and RII.

4. Crystallization of the Fragments of Synthetic DNA
(M. Miller, A. Wlodawer)

The structure of a self-complementary synthetic sequence of DNA: CGCGAATTCGCG has been known for several years as the best example of a B-type double helix. We are interested in obtaining large crystals of this compound in order to conduct a neutron diffraction study which would elucidate more details of the structure of associated water. The largest crystals grown by us so far reach their maximum size of 0.25 mm^3 after about three months and it is necessary to further explore conditions for making them larger.

A related sequence in which adenine is inserted in position 8 (following the sequence ...ATT...) has also been investigated. This sequence is expected to form unmatched base pairing, with the additional residue excluded from the Watson-Crick type double helix (or a loop made of single chain). While such structures are common in nature, they have not yet been observed experimentally. This material crystallizes readily at room temperature but the crystals are small, often are twinned, and their diffraction pattern is disordered. Much better crystals can be grown at 4°C , but they are very unstable during temperature changes and the availability of a proper cooling device will be necessary before they can be fully characterized.

5. Structural Studies of a sweet protein, monellin
(M. Miller, A. Wlodawer)

Monellin, a small protein of molecular weight 9000 daltons, is the second sweetest substance known. Knowledge of its three-dimensional structure would be important to further understanding of the mechanisms of sensory perception and in constructing artificial sweeteners.

Conditions for growth of large crystals of monellin have been optimized. It is necessary to use a macro-seeding method in order to assure reproducibility. This is accomplished by nucleating growth with an addition of a partially dissolved, small crystal to the growth medium. The crystals can reach the final size of about 0.5 mm, but due to their inability to withstand transfers to other solutions they have to be crosslinked in 0.01% glutaraldehyde before use.

Two promising heavy atom derivatives of monellin have been found after extensive search. These two derivatives are made by soaking in either solution of $.25 \text{ mM K}_2\text{Pt}(\text{CNS})_4$ for 24 hours or 0.2 mM KAuCl_4 for 16 hours. X-ray crystallographic data have been collected from several native crystals to the resolution of 4\AA , and three centrosymmetric zones were measured to 3.6\AA from a platinum derivative. Work on locating the heavy atoms using Patterson syntheses is in progress.

6. Joint Neutron and X-ray Structural Refinement of Porcine Insulin
(A. Wlodawer and H. Savage)

Joint X-ray/neutron refinement of insulin has been performed using 2.2 Å neutron data collected on the BT8 flat cone diffractometer at the NBS and 1.5Å x-ray data provided by Dr. G. Dodson, University of York, England. Several different models were calculated, using the X-ray structure as a starting point. The first model was essentially a refinement of the x-ray data alone, lowering the R-factor to 0.148. Next, 24 cycles of joint refinement resulted in a model with R factors of 0.176 and 0.199 respectively for the x-ray and neutron data. The main problem with this model was posed by the movement of solvent atoms out of x-ray density, particularly severe for alternately occupied sites closer than 2Å. Another model was calculated by fixing solvent positions to the initial values and allowing only the atomic positions belonging to the protein to refine. Finally, occupancies of amide hydrogens were refined using neutron data only in order to study hydrogen exchange in the crystals. The R factors in the final model were 0.183 (x-ray) and 0.191 (neutron). The bond lengths deviated by 0.02Å from their ideal values.

The structure of two insulin molecules present in the asymmetric unit was compared in order to correlate the differences with the crystal packing. The two crystallographically distinct molecules differ by the following RMS deviations: 1.88Å in their positions of all non-hydrogen atoms and 2.23Å for all atoms. This apparent discrepancy is due mostly to concerted rearrangements in which the individual elements of secondary structure such as α helices do not vary in an appreciable manner, but their relative positions are strongly influenced by crystal packing forces. The overall average temperature factors for the two molecules were very similar (18.5\AA^2 and 17.0\AA^2). However, large local differences were observed in regions connecting α helices and irregular parts of both termini of the chain B. A number of hydrogen positions could be found directly in the neutron density maps, showing that all histidines were fully protonated, and confirming a direct bond between histidine B10 and zinc, without an intervening hydrogen.

The pattern of protection of amide hydrogens from exchange is strikingly different in insulin than in any other protein studied so far - see Figure 1. The only region of significant protection under experimental conditions employed by us (over four months soak of crystals at pH = 6.5) was found in the center of the helical region in the B chains (residues 14-19 in molecule 1 and 12-19 in molecule 2). No significant protection of amide hydrogens was observed in areas of β sheets. Insulin is comparatively less rigid than proteins such as BPTI and ribonuclease and thus is more susceptible to processes leading to exchange which is in good agreement with the available solution exchange data.

Most of the strongly bound solvent appears to occupy similar positions in the neutron and x-ray $2F_o - F_c$ maps, but there were significant differences in the more disordered regions away from the protein surface.

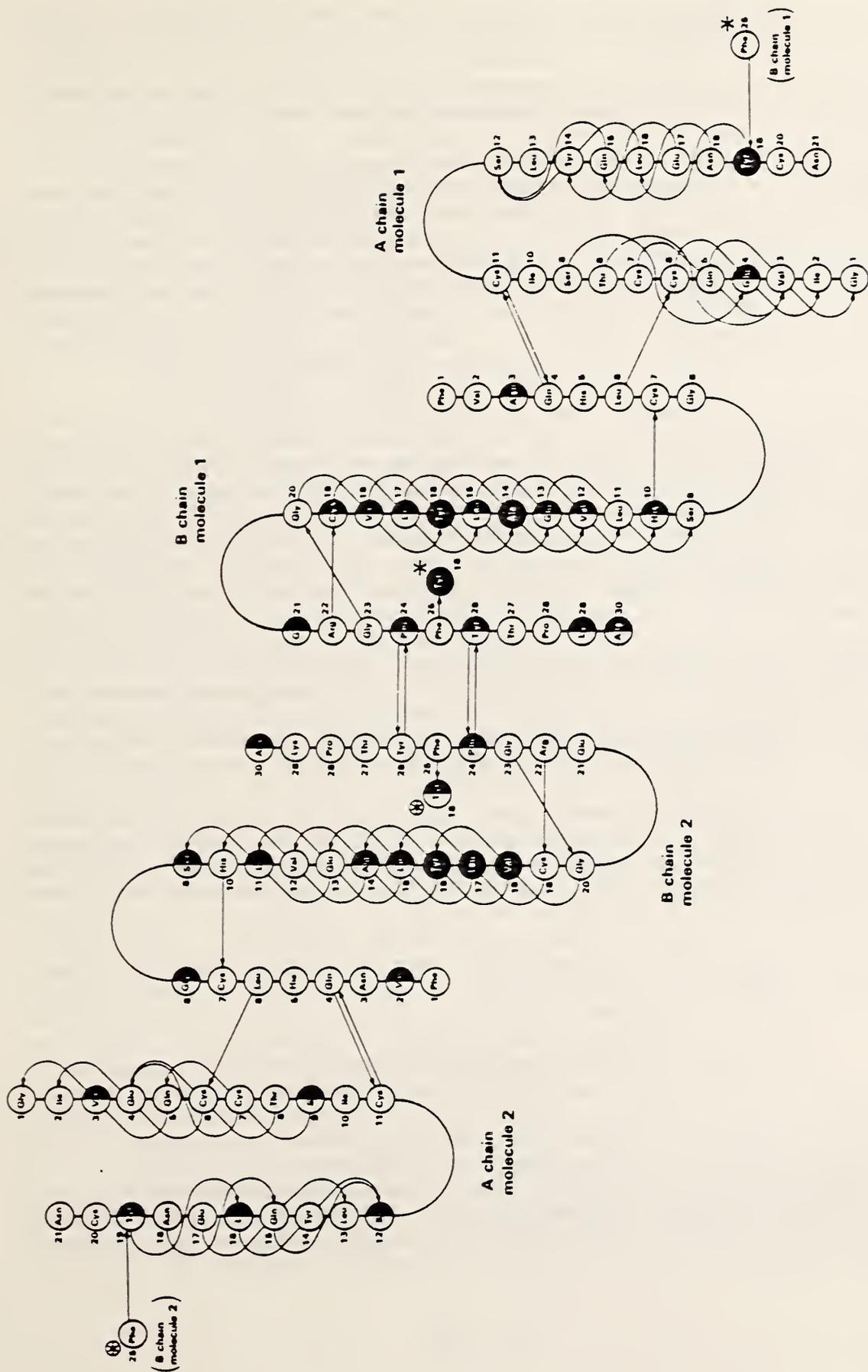


Fig. 1 Diagram of the hydrogen bonds involving the main chain atoms and the level of protection of the amide hydrogens (H exchanged for D): Black residues are fully exchanged, half black/white are partially exchanged and the white residues are unexchanged.

7. Experimental water structure from hydrate crystals
(H. Savage)

Detailed structural characteristics of water structure, both ordered and disordered, have been obtained from a survey of various geometrical parameters around water molecules in the available neutron crystal structures which have been published. These included the ice polymorphs, a large number of small hydrate crystals containing between one and nine waters per asymmetric unit, and some larger hydrate crystals (10-20 waters), in which parts of the solvent regions are disordered. The hydrogen bonding geometries in these structures follow the same trends as those generally observed in known structures, hydrates and non-hydrates. A majority of the waters have either trigonal or tetrahedral coordination, but large distortions of the O-H...O and O...O...O H-bond angles from their 'expected' linear and tetrahedral values occur.

What is not clearly understood about water structure, is how the molecules orient themselves and pack together in more disordered phases such as liquid water. These structural aspects depend critically on the local short range non-bonded contacts which easily outnumber the more attractive ones around a water molecule by more than 24:4. These include O...O, H...O, and H...H non-bonded contacts. In the hydrate crystals, the O...O non-bonded contacts appear to vary around the water oxygens: $\sim 3.5\text{\AA}$ over the lone pair region, $\sim 3.3\text{\AA}$ between the hydrogens and $\sim 3.1\text{\AA}$ between the lone pairs and the hydrogens. The remote H2...O1 contacts of the configuration O1-H1...O2-H2, are seen to have minimum contacts of $\sim 3.1\text{\AA}$ between the lone pairs and the hydrogens. The remote H2...O1 contacts of the configuration O1-H1...O2-H2, are seen to have minimum contacts of $\sim 3.0\text{\AA}$ (O-H distances fixed at 0.8\AA to represent the hydrogen electron density). These minimum contacts are maintained around each water molecule at the expense of distortions in the local H-bond geometries.

Water structure in protein crystals, that have been studied using neutron and x-ray diffraction, is currently being analyzed. A computer program is under development which is designed to formulate water network structures using both the H-bonding and short range non-bonded information as restraints.

8. Statistical Density Modification as an Approximation to Maximum Entropy
(R. W. Harrison)

A simple and quick approximation to the maximum entropy principle can be used in conjunction with phase combination to improve the quality of electron density maps. The distribution of electron density values is required to be Gaussian. When the phases are highly incorrect the distribution is far from Gaussian. A Gaussian distribution corresponds to the distribution found by maximum entropy with the constraint of constant scattering power. With this method the observed electron density values are replaced by values determined by a mapping

between a histogram of the observed density and a Gaussian distribution of the same standard deviation. The mapping is found by requiring that the integrals of the histogram and the Gaussian be identical. The Fourier transform is then calculated and phase combination with any isomorphous replacement data is then used to determine phases for the next cycle.

An electron density map produced by this method was used in solving the structure of Acinetobacter asparaginase in parallel with the method of B. C. Wang. The two maps are comparable in the interior of the protein, but differ considerably on the surface. The map produced by the Gaussian appears to have more electron density at the protein surface than the map produced by solvent flattening. The interpretation of the asparaginase electron density map is described by I. Weber.

9. Structure of DNA Gyrase

(A. Wlodawer, S. Kruger, University of Maryland)

The structure of an enzyme DNA gyrase was investigated by the technique of small angle neutron scattering (SANS). This enzyme acts as a topoisomerase and catalyzes negative supercoiling of DNA coupled to ATP hydrolysis, by allowing a double-stranded DNA segment to pass through an enzyme-bridged, transient double-stranded break. DNA gyrase is composed of two subunits designated A and B with molecular mean close to 100,000 daltons each. The active enzyme is an A₂B₂ tetramer of molecular weight 400,000 daltons.

We have collected SANS data from solutions of each type of subunits, from the active enzyme and from 1:1 complexes of gyrase with a cloned fragment of DNA consisting of about 170 base pairs. All experiments were performed in mixtures of 60% H₂O buffer/ 40% glycerol. Molecular weights of A and B subunits obtained in the experiment were 206,000 and 100,000 daltons respectively (estimated error $\pm 11\%$) indicating that while B subunits make monomeric solutions, A subunits dimerize under the same conditions. Radii of gyration were $43 \pm 3 \text{ \AA}$ and $41 \pm 5 \text{ \AA}$ respectively, indicating compact molecules. Radii of gyration of the holoenzyme and of the gyrase - DNA complexes were both about 53 \AA . Molecular weights of the enzyme and of the complex were measured as 320,000 and 398,000 daltons respectively. While these numbers are lower than expected, their ratio is exactly that expected on the basis of known molecular weights. Their low estimates may be due to errors in the measurements of the concentration of macromolecules and this problem is being investigated. Further experiments will be performed in deuterated solutions, with the aim of investigating the arrangement of DNA and protein in the complex.

10. Future Plans

The main thrust in the next year will be to complete the x-ray data collection facility in order to provide us with in-house capabilities in that field. We will build, from commercially available parts, a unique diffractometer equipped with a two-dimensional position sensitive detector which will be the best available. It will enable us to collect high

resolution x-ray diffraction data in temperatures ranging from -65°C to +80°C in a very short time. We shall continue to convert programs to run on the IBM 4381 and develop programs for the Cyber 205.

We are planning to continue most of the current research programs and to start several new ones. We hope to complete work on the structure of Acinetobacter asparaginase and to compute high resolution maps of the Pseudomonas enzyme. We will attempt to solve the structures of one or more CAP mutants and hope to produce an electron density map of monellin. We will attempt to crystallize other available proteins and DNA. We hope to complete the neutron investigation of insulin and to initiate neutron investigation of Z-DNA and of an enzyme elastase. We will continue theoretical work on the development of the technique of maximum entropy as applied to electron density maps. Since the currently available flux on the small-angle neutron scattering instrument at NBS is insufficient to complete the investigation of DNA gyrase, we will collect necessary data in Grenoble, France.

3. CHEMICAL THERMODYNAMIC MEASUREMENTS

E. S. Domalski, S. S. Bruce, T. J. Buckley, J. Colbert, H. DeVoe
D. A. Ditmars, D. R. Kirklin, P. Thompson, S. P. Wasik

A. Large Sample Combustion Calorimetry

(E. S. Domalski, D. R. Kirklin, J. C. Colbert, K. L. Churney, A. E. Ledford, S. S. Bruce, and T. J. Buckley)

This research is being performed in support of the Research Conservation Recovery Act. Its purpose is to provide measurement methods, standards and data for establishing heating values of a variety of municipal solid wastes and for assessing the environmental impact of using these waste streams for generating electrical power.

1. The Calorific Value Problem

Incinerator-boiler systems used to dispose of municipal solid waste (MSW) are bought and sold on the basis of thermal specifications. To determine whether a system meets its thermal specifications, the calorific value of the input waste stream must be known. During FY 1984, we completed a study showing that, using suitable procedures, representative gram-size test samples can be prepared from a 2.5 kg sampling increment. (The set of such increments is used to characterize the calorific value of the waste stream fed to an incineration.) These results settled the dispute among combustion engineers concerning whether gram-size test samples are too small to characterize a multi-ton pile of municipal solid waste

A second problem with existing calorific value test methods is that combustion results are for complete combustion of the organic fraction of MSW to CO_2 , H_2O etc. To apply these results to an incinerator, they must be corrected for the products of incomplete combustion that occur in real-world waste to energy systems. Currently no data are available for validating methods either for the measurement of the degree of incomplete combustion or the calculation of appropriate calorific corrections. To rectify this situation, a study of the energy balance for incompletely combusted waste was started in FY85. During the first half of the year, eleven preliminary experiments, with associated apparatus development, were carried out in the 2.5 kg flow calorimeter. Pellets of pure (microcrystalline) cellulose or synthetic refuse-derived-fuel (RDF) were combusted in O_2/N_2 gas mixtures of 100, 50, 35, 21 and 17 mol% O_2 . The synthetic RDF was made from a mixture of cellulose and 20 mass % inert material (silica and alumina). A goal of the study was to determine the conditions for incomplete combustion of the cellulose, alone or as a component, to gaseous products and a solid char. The char is required to have a mass sufficient for subsequent elemental and calorific value analysis. Cellulose was used in order to have a reproducible enthalpy of

combustion (i.e. to CO₂, H₂O, etc.). The material was burned in pellet form rather than in loose form to simplify quantitative collection of ash and char.

The principal results of the study were:

(a) Appreciable (>40g) char and (usually) no unburned cellulose was produced by combustion of synthetic RDF at 21 mol % oxygen. Part of the gas supplied to the combustor was preheated (by electrical heating) to 100°C to prevent appreciable amounts of unburned cellulose being present in the combustion residue (ash). The sample did not completely char at 17% oxygen and the amount of char formed at 35% or higher oxygen concentrations was small (<2 g). The amount of char is evidently dependent on the inert material particle size. The amount cited above for 21% oxygen is for 650-800 μm particle size silica. Negligible char (<29) is formed at 21% oxygen using a 50μm particle size of inert material consisting of 50:50 silica and alumina.

(b) Hot gaseous hydrocarbons leaving the combustor were monitored using a heated sample line (>105°C) and a flame ionization detector. Provision for correction of the associated heat loss of the calorimeter is accomplished by a thermocouple to determine the temperature of the sample gas as it leaves the calorimeter, a flow meter, and calculation of gas composition obtained by other measurements.

A final series of combustion measurements (ten as of 8/19/85) for comparison of energy and mass balances at 100, 50, 35, and 21 mole percent oxygen is in progress.

During FY 1986, we plan to complete the elemental and calorific value analysis of the ash residue (i.e. char), the calculation, and the evaluation of the energy balance study.

2. Organo-Chlorine Compounds in MSW

During the past decade, dioxins and difurans have been found in the ppt to ppb range in the fly ash and flue gas of a number of incinerators in the U.S. and Europe. The resulting public alarm has seriously slowed or even stopped construction or operation of many waste to energy plants. The main methods proposed for reducing the dioxin and difuran emissions are removal of the responsible components of the waste and "proper" design and/or operation of the incinerator. Currently, the quantitative data bearing on these proposals is meager. As of 1984, we were aware of only one study of the chlorine content of the various components of MSW. No consensus concerning "proper" design and/or operation of incinerators to reduce dioxin emissions exists because of lack of data and theory on the formation/destruction of organo-chlorine appropriate to incinerator combustion conditions. In response to this situation, the following two studies are being carried out.

(a) Chlorine Content of MSW

During the FY 1984, sampling of MSW was carried out at two sites, each for periods of five days. Five days samples were obtained from Baltimore County, Maryland, and five days samples from Brooklyn, New York to provide some idea of differences between MSW from different areas. About 13-20 kg of refuse was sampled daily from the output of the primary shredder of the Baltimore County Resource Recovery Facility in Cockeysville, Maryland. The New York samples were obtained by removing five to seven increments of MSW on each of five days from the receiving pit of the Green Point Incinerator in Brooklyn, New York. All samples were dried and hand sorted into combustible components (paper, hard and soft plastics, textiles, wood/vegetable matter, and fines/sweepings) and non-combustible components (glass, metals). Each of the combustible components was processed to < 2 mm particle size, blended (i.e., homogenized), and sampled for analysis to determine water-soluble chlorine and total chlorine content. A reconstituted sample of each of the ten days waste was prepared to determine the chlorine and the total sulfur content of the original (i.e., unsorted) MSW. Analytical determinations were completed.

During FY 1985, the results of the study were evaluated and published. The principal results are as follows:

- (1) All combustible components contain chlorine.
- (2) The paper and plastic fractions contain the major portion of the chlorine content.
- (3) Most of the water soluble chlorine content is found in the paper fraction.
- (4) Most of the water insoluble chlorine content is found in the plastic fraction.
- (5) In the MSW from Baltimore County, MD, the total chlorine content is 0.45% on a dry basis. About half of the chlorine is from the paper, one quarter is from the plastics, and the other quarter is from the remaining components. The mass percent of the paper and plastics in the original, dry waste stream were about 60% and 7%, respectively.
- (6) In the MSW from Brooklyn, NY, the total chlorine content is 0.89% on a dry basis. About half is from the plastics, one quarter from the paper, and the other quarter is from the remaining components. The mass percent of the paper and plastics in the original, dry waste stream were about 47% and 11%, respectively.

- (7) Removal of the plastic fraction from either waste stream reduces the total chlorine content of the MSW from Baltimore County, MD, from 0.45 to 0.33% and the waste from Brooklyn, NY, from 0.89 to 0.50%.

During FY 1986, we propose, if time and funding permit us, to initiate analysis of the sorted components of the above two sources of waste for the type and amount of chloro-organics.

- (b) Threshold Conditions for Formation/Destruction of Organo-chlorine Compounds

A study to determine the threshold conditions for the formation and/or destruction of organo-chlorine compounds in the combustion of MSW was initiated at the end of FY 1984. During the FY 1985, equipment construction and measurement procedure appropriate to this study were carried out during the course of our study of the energy balance for incomplete combustion discussed in section 3.A.1. Our purpose is to determine if we can reproducibly form and/or destroy organo-chlorine compounds including dioxins in the 2.5 kg capacity flow calorimeter and, if so, whether the combustion conditions (used in the energy study) can be sufficiently well characterized to admit application of the results in the threshold study to incinerator combustion conditions. The following was accomplished:

- (1) A gas trap for trapping out gaseous species having dew points $> -10^{\circ}\text{C}$ and a charcoal scrubber have been installed in the main stream of the product gas exit line. The trap removes dioxins to the tens of ppt level or less, and the scrubber finishes the removal of organo-chlorine compounds before the product gas enters the laboratory exhaust system.

- (2) An EPA modified method 5 gas and particulate sampling train for chlorinated organics was built. The product gases are sampled through a heated ($> 105^{\circ}\text{C}$) line from the calorimeter combustor. Particulates are trapped on Zitex filters and subsequently gaseous chlorinated organics are adsorbed on XAD-2 resin.

- (3) To date, two combustions of synthetic RDF doped with polyvinyl chloride (PVC) have been run: one 2.5 kg pellet with 1.5 mass % PVC in 35 mol % oxygen and a 3.7 kg pellet with 0.8 mole % PVC in 21 mol % oxygen. Procedures for extraction of the sampling train filters and the XAD-2 resin and isolation of various polychlorinated dibenzo-p-dioxins and then chlorinated organic components using chromatographic means were developed and carried out by S. Chesler et. al. of the NBS Organic Analytical Research Division. Qualitative analyses using gas chromatography with an electron capture detector were carried out for the second combustion run. Chlorinated benzenes, (tetra, penta, and hexa), chlorinated phenols (2, 4, 6 trichloro) and strong indications of a number of the polychlorinated biphenyl congeners (e.g. PCB 3, 28, 52, 101, 153) were found.

(4) Computer control of the gas mixture supplied to the combustor of the flow calorimeter (air doped with O₂ or N₂ for 50 to 97 mol% O₂) was implemented and software was developed to evaluate combustion conditions as a function of time.

During FY 1986, we plan to complete the preliminary study of the combustion of pellets of synthetic RDF doped with PVC and with an inorganic chloride (and possibly both). Combustion conditions will be modified to improve their definition as needed. A final study would be initiated that would involve variations in MSW composition, including both synthetic and real world RDF doped with chlorine compounds.

Financial support for this activity comes from the U. S. Department of Energy, Biofuels and Municipal Waste Technology Division.

B. Certification of Combustion Calorimetry Standard Reference Materials (J. C. Colbert and D. R. Kirklin)

The precision bomb calorimetry activities include the certification of primary and secondary calorimetric standards that are used worldwide to calibrate and check calorimetric and analytical procedures. The primary calorimetric standard is benzoic acid, which has been available from NBS since the 1920's and which remains one of the top selling standard reference materials (SRM's). Secondary calorimetric standards are needed for compounds which contain elements other than carbon, hydrogen and oxygen and therefore require slightly modified calorimetric procedures to obtain accurate and meaningful data.

Standard Reference Material certificates were prepared for three calorimetric standards. Thianthrene was certified as an organic sulfur standard. Nicotinic acid and urea were certified as low nitrogen and high nitrogen content organic nitrogen standards. A Synthetic Refuse Derived Fuel has also been certified. In addition, triphenyl phosphine oxide was studied as a possible organic phosphorous standard.

1. Certification of the Energy of Combustion of Thianthrene (D. R. Kirklin)

Thianthrene was certified as a test substance for use in checking calorimetric apparatus, analytical procedures and the calculations utilized in oxygen bomb calorimetry of organic sulfur compounds. The actual measurements were performed during fiscal year 1984 and the certificate was prepared during fiscal year 1985. The certified value was $-33,480.4 \pm 7.4$ J/g at 298.15 K.

2. Certification of the Energy of Combustion of Nicotinic Acid and Urea
(D. R. Kirklin)

During the month of January 1985, measurements were made on SRM 2151 (Nicotinic Acid) and SRM 2152 (Urea) to check the certified energy of combustion at 25°C. The following values in MJ/kg were obtained.

<u>Nicotinic Acid (SRM 2151)</u>	<u>Urea (SRM 2151)</u>
22.188	10.534
22.187	10.539
22.188	10.533
<hr/>	
Mean: 22.188	10.535

These values were obtained at 28°C and when calculated to 25°C are within the uncertainty limits of the certified energy of combustion values. The certified values for nicotinic acid and urea are 10.536 ± 0.003 and 22.185 ± 0.005 MJ/kg, respectively.

All of the measurements were made on samples which had been dried to a constant weight. In addition, the number of grams of water placed in the bomb was equal to 30 times the volume of the bomb in cubic decimeters (liters).

3. Investigation of Triphenyl Phosphine Oxide as an Organic Phosphorous Calorimetric Standard
(D. R. Kirklin)

This calorimetric standard is needed to evaluate calorimetric and analytical procedures utilized in organic phosphorous studies. Triphenyl phosphine oxide has been suggested as a suitable calorimetric phosphorous standard because it can readily be obtained in a state of high purity and is a non-hygroscopic substance that is very stable under ambient conditions. Triphenyl phosphine oxide should exhibit difficulties similar to other "unknown" phosphorous compounds and therefore should allow experimenters to evaluate their procedures. A set of six measurements yielded a specific energy of combustion of $35,788.15 \pm 5.06$ J/g with a percent coefficient of variance of 0.007%.

4. Calorimetric Update on SRM Coals 2682, 2683, 2684 and 2685.
(J. C. Colbert)

The annual calorimetric update on SRM Coals 2682, 2683, 2684 and 2685 was performed to determine if there has been any change in the calorific value of these coals due to sample degradation as a result of aging and oxidation.

Sixteen unopened bottles of the coals were received from the OSRM, four of each SRM. One measurement was made for calorific value and one for residual moisture. The original certified value for sulfur and ash were used in making the calculations since these constituents remain constant with time. All of the measurements were performed in random order as established in a sampling procedure and run protocol designed by R. C. Paule, NML Statistician.

The results were statistically evaluated and as was expected minor degradation of the calorific values had occurred. The SRM certificate was revised to reflect these changes in the calorific values along with the new uncertainties and were included on the revised certificate of February, 1985.

The uncertainty includes the observed variability within and between HHV2 (calorific value-moisture free) measurements, any observed sample heterogeneities, and an allowance for sample degradation equivalent to one year's degradation.

5. Certification of Synthetic Refuse-Derived Fuel, SRM 1657.
(J. C. Colbert)

Certification of the Synthetic Refuse-Derived Fuel, SRM 1657, was completed this fiscal year with the certificate issued in March, 1985. This SRM consists of three components blended to resemble a sample of refuse-derived fuel. The composition of the SRM is approximately 80 mass percent microcrystalline cellulose, 15 mass percent silica, and 5 mass percent alumina.

Measurements have been performed on the bulk and bottled synthetic RDF. The measurements on the bottled material consisted of moisture, ash and calorific value. Five batches, each consisting of six samples were measured for moisture and ash. Selected sample bottles of the same material were used for the bomb calorimetric measurements. A total of fourteen bomb calorimetric measurements were made. Statistically significant bottle-to-bottle heterogeneity was observed for the measured properties. The dry ash value for the bottled material of 20.34% was appreciably lower than the 20.67% value observed for the bulk material that was run in FY 84. In an effort to confirm these values a side-by-side comparison of the bulk and bottled material was made. Determinations for residual moisture and ash were performed. The results clearly showed that the 0.33% difference was statistically significant. The reason for this difference is not understood but could be attributed to a small loss of the ash in the bottling procedure. The certificate values are for the bottled material only and are appropriate since it is the bottled material which is sold. The certificate value for the dry ash is 20.34 ± 0.54 mass percent.

In FY 86 the enthalpy of combustion of benzoic acid will be recertified. Benzoic acid is a best seller of the SRM program and periodically needs to be recertified as stocks run out. Enthalpies of combustion of oils and coals will also be measured for certification as SRM'S.

C. Estimation Methods and Combustion Calorimetry on Organic Phosphorous Compounds
(D. R. Kirklin and E. S. Domalski)

Precise enthalpies of formation are not available for important industrial and biochemical compounds that contain phosphorus. Experimental determination for many of these compounds is not feasible because of their toxicity or their limited availability. The objective of this project is to develop correlation and estimation schemes which are needed to predict enthalpies of formation at 298 K for compounds having no reported experimental values.

A table of reaction enthalpies at 298 K has been compiled for some 50 organic phosphorous compounds. Group contribution values which follow the additivity principle have been derived from the evaluated data. An experimental calorimetric program to determine the thermochemical properties of key organic phosphorous compounds has been formulated as a result of these correlation and estimation schemes.

The first objective of the experimental program is to establish a calorimetric standard for the combustion of organic phosphorous compounds. The calorimetric standard is necessary to evaluate calorimetric and analytical procedures utilized in organic phosphorous studies. Triphenyl phosphine oxide has been suggested as a suitable calorimetric phosphorous standard because it can be readily obtained in a high state of purity and is a non-hygroscopic substance that is very stable under ambient conditions. Triphenyl phosphine oxide should exhibit difficulties similar to other "unknown" phosphorous compounds and therefore should allow experimenters to evaluate their procedures.

Over twenty measurements of the enthalpy of combustion of triphenyl phosphine oxide were made in the NBS adiabatic rotating bomb calorimeter. The rotating feature is especially important because one of the major problems associated with combustion studies of these compounds is the attainment of a homogeneous bomb solution to ensure that the acids of phosphorus with large energies of dilution are not formed in various concentrations in different parts of the bomb. The attainment of complete combustion was also a major problem. Oxides of phosphorus and their acids tend to condense on the burning compound causing significant amounts of carbon residue to remain in the crucible. Another problem encountered was that many of the usual crucible materials were readily attacked during the combustion process. Platinum and quartz crucibles were readily attacked. Gold crucibles showed no signs of attack but sometimes melted when the combustion reaction proceeded too vigorously. A stoichiometric accounting of the combustion reaction requires a complete determination of the

substances present in the initial and final states. The combustion products may contain a mixture of several oxyacids of phosphorus which must be quantitatively measured. A set of six of the best measurements yielded a specific energy of combustion of $35\,778.15 \pm 5.06$ J/g with a percent coefficient of variance of 0.007%. However, this value is about 0.03% below the best value in the literature. We believe that this discrepancy is due to our inability to quantitatively determine the amount of carbon residue of the combustion reaction.

Future plans are to run another set of approximately 7 combustion experiments under conditions which will produce insignificant quantities of carbon residue and determine the extent of reaction by analyzing the CO_2 produced in the combustion of the sample. After establishment of triphenyl phosphine oxide as a secondary combustion calorimetry standard, several key organic phosphorous compounds will be investigated. Proposed compounds are tricyano phosphine and triphenyl phosphine.

Funding for this research comes from the U. S. Army, Chemical Research and Development Center, Aberdeen, MD.

D. Bomb Calorimetric Measurements of 2-Deoxy-D-Ribose (J. C. Colbert and E. S. Domalski)

Combustion bomb calorimetric measurements were completed on a sample of 2-deoxy-D-ribose in FY 85. The molar enthalpy of combustion at 301.15 K for seven experiments is $\Delta_c H = -18842.34 \text{ J} \pm 1.20$ (1SDM) kJ mol^{-1} . The measurements were carried out with the aid of an auxiliary substance, benzoic acid, which acts as a catalyst in the ignition of the sample. Initially, measurements were performed by encapsulating the pellets in a small polyethylene bag. The sugar is slightly hygroscopic and the polyethylene B served to protect the sample from moisture absorption. All samples were encapsulated in a dry box. This method was abandoned since there was appreciable scatter in the data that was found to be attributable to the polyethylene.

The measurements were finally performed using samples that were dried in a 25°C vacuum oven. Measurements on moisture content made by the Karl Fischer Method were used to correct the sample mass to a dry basis.

NMR sample characterization techniques indicate that the anomeric content of the sugar is the β -pyranose and δ -pyranose form in the amounts of 65% and 35%, respectively. This anomeric content is assumed to exist in the solid as well as in solution, which is the method in which these NMR measurements were made. Time dependence studies of equilibrated solutions of the sugar in DMSO-d_6 , when extrapolated to time-zero, support this assumptions.

CO_2 analysis was performed on the bomb combustion products to determine the sample purity. The gaseous products of combustion were released from the bomb and passed through absorption tubes containing

Ascarite, magnesium perchlorate and P_2O_5 . The amount of CO_2 was then determined gravimetrically. The analysis for CO_2 indicates a purity for 2-deoxy-D-ribose of $99.93 \pm .03\%$ (sd).

In FY 86 the enthalpy of combustion of either hexaglycine or hexaalanine will be determined. Both these peptides are straight chain like molecules. This experiment is being done to establish the feasibility of an "additivity approach" to the estimation of enthalpies of formation of simple peptides using the enthalpy of formation of the amino acids residues and an enthalpy of formation of the peptide bond.

E. Drop Calorimetry of Non-Reacting Systems Below 2800K
(D. A. Ditmars)

This activity is a continuation of a calorimetric research program whose goals are:

1. to obtain accurate thermodynamic data on non-reacting refractory materials in either the solid or liquid state up to 2800 K.
2. to measure specific heat at temperatures above 273 K of well-characterized materials of the highest attainable purity for which existing C_p data are insufficient or in conflict and which are:
(a) critical to energy and space related technology, or (b) especially suited as models on which to test refined lattice-dynamic calculation of thermodynamic properties.
3. to produce and support high-temperature calorimetric standard reference materials (SRM's) for heat capacity and for differential thermal analysis (DTA) calorimetric measurements.

The number of facilities, nationally, which can sustain programs of high-temperature calorimetric research is seriously diminishing at a time of increasing needs for just the data produced through this type of investigation. There is a constant demand for thermodynamic data on new materials capable of functioning acceptably in the harsh environments associated with space propulsion systems or upon re-entry, new energy technologies and defense-generated needs for materials to enable space systems to withstand overt aggression. Also, the existing thermodynamic data on some elements is often not accurate enough to allow a meaningful test of theories which have recently been formulated to calculate thermodynamic functions directly.

The Chemical Thermodynamics Division has available two operative precision drop calorimeters for the ranges 273-1200 K (isothermal, phase-change calorimeter) and 1200-2800 K (adiabatic receiving calorimeter). These are being used in research intended to provide calorimetric measurements at the highest accuracy on materials related to the high-temperature applications mentioned above. Every effort is made to coordinate this research with that of another NBS facility (very-high-temperature pulse calorimeter) in order to provide the capacity for

continuous coverage of high-temperature thermodynamic studies up to 5000 K or above on especially important systems. We have in addition an operative high-temperature discrete-heating adiabatic calorimeter (300-800 K) and we maintain in reserve a low-temperature (4-300 K) adiabatic calorimeter for possible future research needs.

In order that NBS thermal data and that of other high-temperature investigations can be fairly intercompared and assessed for accuracy, we maintain a continuing effort to update or extend the range of coverage of high-temperature standard reference materials. In recognition of the growing need for accurate DTA temperature and enthalpy standards we attempt to identify systems whose thermal properties can be measured by both conventional calorimetric and DTA techniques.

We continued our investigation of boron nitride. This material, exists in two phases, hexagonal and cubic. The hexagonal phase is a layered structure akin to the graphite structure and is widely used in the fabrication of components for service at high temperatures in chemically aggressive environments, particularly where high resistance to mechanical and thermal shock are important. We have prepared a specimen and commenced relative enthalpy measurements in the range 1200-2800 K.

In fiscal year 1984, our research on pure metals for which the existing tabulated thermodynamic functions are known to be in error, included calcium and strontium. A sample of calcium, upon which enthalpy measurements in the range 273 to 715 K had previously been completed, was submitted for analysis and found to contain in excess of 2 mole percent CaO. This impurity was qualitatively confirmed in the behavior of the sample in Thermal Analysis. The sample was re-distilled in the Metallurgy Department of Iowa State University, thereby reducing the oxygen concentration by a factor of 10 and the hydrogen concentration by a factor of 2. A portion of the purified sample was loaded into an adiabatic low-temperature calorimeter at the U. S. Geological Survey in Reston, VA and its heat capacity measured from 4 to 380 K. Another portion was encapsulated and its relative enthalpy measured in the bcc stability range, 715 to 1112 K. The heat of the fcc-bcc transition at 715 K was also measured for both the original sample and the purified sample. Preliminary analysis of the heat capacity data confirms that existing C_p data compilations for calcium can be in error by as much as 30 percent.

A specimen of purified strontium was obtained on loan from Prof. Westrum of the University of Michigan Chemistry Department. There exist no published high-temperature data on this element. We have measured the heat capacity of the fcc phase up to 812 K, the temperature of the fcc/bcc transition.

In fiscal year 1986 we plan to complete measurements on BN (hex) and combine this data with our existing data below 1200K. We plan to commence a study of pure zirconia, yttria-stabilized zirconia and/or zirconia/alumina ceramics in order to generate the thermodynamic data necessary to AFOSR investigators working in the modelling of

transformation-roughened ceramic systems and in the calculation and prediction of multi-component ceramic phase diagrams. We plan also as time allows to extend our strontium measurements into the bcc phase above 812 K and to determine the enthalpy change on melting of our pure calcium sample. A guest worker from Brock University is coming to NBS to measure the heat capacity of copper up to its melting point. This data is to be used to verify theoretical models for calculating thermodynamic properties of bcc metals.

Financial support for this work has come from the U.S. Department of Defense, Air Force Office of Scientific Research.

F. Weak Interactions in Model Enzyme-Substrate Systems

(P. T. Thompson, R. H. Wood, D. Smith-Magowan, S. P. Wasik, and H. Devoe)

Intra- and intermolecular interactions between functional groups and other moieties of molecules dissolved in an aqueous medium play crucial roles in a variety of properties and reactions. For example, the tertiary structure of a globular protein is determined by non-bonded intramolecular interactions, as well as by hydrogen bonding. The binding of a substrate molecule to an enzyme also depends on these interactions. The objective of this research is to measure the Gibbs energy, enthalpy and entropy components of the interaction of several hydrophobic solutes with a variety of molecules dissolved in water, and to analyze these quantities in terms of either group-group interactions or solute dimerization. These data are needed for understanding the physical basis of hydrophobic effects, for predicting various solubility and binding properties, and for refining empirical potential functions for the pairwise interaction of molecular groups immersed in water. The information is of great interest to technologies which deal with stability and binding effects involving macromolecules, such as enzyme-substrate specificity, to researchers in the area of molecular recognition and host/guest chemistry when hydrophobic groups are involved, and to those who calculate aqueous properties by Monte Carlo and molecular dynamics computations.

The research underway is based upon measurements of the solubility of a solid hydrophobic compounds in aqueous solutions containing a second solute (the cosolute). At a given temperature and pressure, the chemical potential of the dissolved hydrophobic solute in the saturated solution is constant regardless of the concentration of the cosolute. Therefore, the effect on the solubility of changing the cosolute concentration can be interpreted as an activity coefficient effect; or, alternatively, as a free energy of interaction between the hydrophobic molecule and the cosolute species. The data (solubility versus molality of cosolute) from measurements with cosolutes containing different functional groups is treated by the method of Savage and Wood to provide the free energies of group-group interactions. The temperature dependence of these free energy parameters yields the enthalpy and entropy components of the interactions.

The aqueous solubilities are measured using a coupled-column liquid chromatography (CCLC) method developed at NBS. A generator column is packed with crystals of the solute, or with a chromatographic solid support coated with the solute. Pure water or an aqueous solution of the cosolute is pumped through the column to saturate the solution with the solute. The solute concentration in the aqueous phase is found by extracting the solute from a known volume onto an extractor column, and eluting this solute onto a reverse phase analytical column for determination by HPLC.

An automated version of the CCLC apparatus has been developed and used to measure the solubilities of naphthalene and pyrene in aqueous butanol solutions. The automated system includes control by a microcomputer of temperature, valves, HPLC pumps, and integrator, together with provision for automatically changing the cosolute solution used as solvent. Recently, this apparatus was moved to a new location and reassembled. Its performance has been thoroughly evaluated and several changes expected to improve the precision of the measurements are being incorporated.

The solubility of naphthalene, pyrene, anthracene, phenanthrene, and tetracene in the presence of aqueous butanol, cyclohexanol, myoinositol and mannitol are planned as the next experiments. Later it is expected to proceed with the solubility of these same solutes with cosolutes containing aromatic rings with hydroxyl and amine functional groups. Eventually it is planned to include cosolutes containing aromatic rings with hydroxyl and amine functional groups. Eventually it is planned to include cosolutes containing nitrogen heterocyclic rings with amine and carbonyl groups in order to explore stacking interactions of the type encountered in aqueous nucleic acid systems.

These results will be analyzed to yield the pairwise Gibbs energy of the solute-cosolute interactions and further broken down into group-group interactions according to the Savage-Wood additivity principle [J. Solution Chem. 5, 733 (1976)]. This principle assumes that the total interaction between two solute molecules is the sum of all possible group-group interactions. From these results it should be possible to construct a hydrophobicity scale which, being based on actual hydrophobic interactions would be an improvement over existing scales which have been calculated from data on the transfer of groups from water to the vapor phase or to a nonaqueous solvent. These results could also be used to interpret dimerization constants of polycyclic aromatic hydrocarbons in water, e.g. of the type observed for benzene by Tucker and Christian [J. Phys. Chem. 83, 426 (1979)].

A related but separate project is to calculate aqueous solute-solute Gibbs energies directly by evaluation of the integrals contained in the cluster expansion expression for the second virial coefficient of solute-solute interaction. Results obtained from calculations on a carefully chosen experimental data set including alcohols and polyols has led to preliminary values of the parameters in the square-well potential functions of the $\text{CH}_2\text{--CH}_2$, $\text{CH}_2\text{--OH}$, and OH--OH interactions. The model is

crude and some numerical approximations are necessary, but results obtained so far indicate that it will be possible to predict aqueous solute-solute interactions on a theoretically sound, albeit simplified, basis. This work is in progress, using the new NBS computer facilities, and plans are being made to extend the results to include polysaccharide interactions and cyclodextrin-inclusion compound complexes. Because of the known enzymatic and transporting capabilities of the cyclodextrins in real biological systems, the latter study would be especially significant and interesting.

4. CHEMICAL THERMODYNAMIC DATA ACTIVITIES

D. Garvin, D. Bickham, D. Cockrell, P. Fagan, C. Jackson
T. Jobe, D. Neumann, D. Smith-Magowan

The goal of this work is to provide reliable values of thermochemical and thermodynamic properties of chemicals, both inorganic and organic. Because of the widely differing needs of users, emphasis is placed in this work on generic information and methods of wide applicability. Two data centers carry on the work: the Chemical Thermodynamics Data Center (CTDC) and the Electrolyte Data Center (ELDC). Their work is interlinked and is reported here by topic, not by organization. The work of both data centers is being extended by extra-mural collaborations.

The data group now consists of three and one-half thermochemists, a computer system manager, two computer programmers, a technical information specialist and a clerk. In addition four thermochemists do special tasks under contract.

The Chemical Thermodynamics Data Center (CTDC) emphasizes evaluation of data leading to formation properties (enthalpy and Gibbs energy) and entropy at 298.15 K for as wide a range of chemicals as possible. The resulting recommendations are published in NBS series, the Journal of Physical and Chemical Reference Data, Handbooks, publications of CODATA and ASTM, and by other agencies and professional societies such as the Design Institute for Physical Properties Data (DIPPR) of the American Institute of Chemical Engineers. In addition, the Center prepares an annual current awareness index to inorganic thermochemistry and answers requests for information. This work is based on the Center's subject index to the world's literature on chemical thermodynamics and molecular properties, which is updated each year.

CTDC also manages the computer facilities that also are used by the Chemical Kinetics and Ion Energetics Data Centers and the Sputtering Data Project in the Surface Science Division. This work includes day-to-day operation of a mini-computer system, selection and testing of new hardware and software, system and applications programming, and training of users.

During FY1985, emphasis has been on (1) collaborative work--the CODATA Thermodynamic Tables, the CODATA Key Values for Thermodynamics, and the OECD Nuclear Waste Disposal Study, (2) energy use--flue gas cleanup for coal fired power plants and data for biomass, (3) information services, and, (4) development of new automated tools for data evaluation and data base management.

The demands for thermodynamic data continue to come from all parts of science and industry. Current requests for information show no pattern other than interests in specific compounds. Symposia on thermodynamics, however, indicate general interests in high temperature processing of solids, vapor transport, mineral assemblages, hydrothermal reactions, and, in the organic

chemical area, continued interest in fluid mixtures and vapor pressures. The geochemists are among the most avid current customers for thermochemical data. It is noteworthy that all of these applications require thermodynamic data as a function of temperature, and at times, pressure.

The Electrolyte Data Center (ELDC) provides evaluated data on the physical and chemical properties of electrolyte solutions to a diverse body of users in the scientific and technical communities. Data are disseminated through contributions to scientific publications, information services in response to telephone and letter inquiries, and through collaboration with the NBS Corrosion Data Center.

The ubiquity of technical problems involving electrolyte solutions gives the Electrolyte Data Center an extremely broad constituency to serve. In the past, programs have been conducted that addressed needs in such diverse areas as water pollution, battery design and development, corrosion and deposition problems in steam power cycles, geochemistry, oceanography, natural gas and oil exploration and processing, other energy technologies, as well as basic laboratory study in virtually every physical science discipline. Emerging technologies such as electronics and biotechnology present challenging new applications as they develop increasingly sophisticated processing and separation techniques using aqueous fluids of increasing chemical complexity.

The Center conducts research into improved or new methodologies for the correlation and estimation of solution properties and presents the results of such research to interested forums.

Effort in FY 1985 was directed to activities that fall in three categories: (1) Studies of the thermodynamics of aqueous electrolytes, (2) development of data evaluation methods, and (3) thermochemistry of biochemical equilibria. These are described later.

A. Thermochemical Data Evaluation for Inorganic Systems
(D. Garvin, V.B. Parker)

The data evaluation effort this year involved participation in three cooperative international programs. NBS evaluates data, coordinates work, advises on procedures and provides support services for each.

1. CODATA Thermodynamic Tables System

A comprehensive set of thermodynamic tables on selected compounds of calcium has been completed on a collaborative program sponsored by CODATA (Committee on Data for Science and Technology of the International Council of Scientific Unions). These tables, prepared as the first of an international series, include thermal functions, thermochemistry, an alloy, a fused salt and an aqueous solution system. Extensively documented, entirely automated, this 200 page book is now being reviewed and prepared for publication late in 1985.

The work has been done in five laboratories: NBS, Dow Chemical (JANAF), AERE Harwell, U.K., ENSEEG, Grenoble, France, and the Akad. Nauk Thermocenter, Moscow, USSR.

The NBS data centers provided: (1) selected values at 298.15 K for thermochemical properties of 68 compounds, (2) thermodynamic properties for the $\text{CaCl}_2\text{-H}_2\text{O}$ system, 298.15-373.15 K, (3) 394 evaluations of thermochemical measurements, (4) quality controls to assure consistency among all tables, and (5) editorial supervision (with D.D. Wagman, R. L. Nuttall).

2. Key Values for Thermodynamics

The "CODATA Key Values for Thermodynamics" have been completed and are being edited for publication late in 1985. This final report of a CODATA Task Group has been written by D.D. Wagman, V.A. Medvedev and J.D. Cox. The report covers 150 substances (53 elements and one or two compounds of each) that are central to thermodynamic measurements and data evaluations. These recommendations are backed up by 100 tables of thermal functions, extensive documentation, a catalog of measurements related to the thermochemistry of aqueous ions and a 2000 item bibliography. These reference data are expected to be the standards used throughout chemical thermodynamics for the next 10 years. NBS data centers have provided analyses of data, particularly for aqueous species, and editorial services.

3. Data for iron compounds and nuclear waste storage systems

Two new thermochemical data projects have been undertaken. One is the thermochemistry of compounds of iron. The objective is to provide an up-to-date thermodynamic data base for use in process calculations involving this economically important element and its compounds. The evaluation is being done for the CODATA Thermodynamic Tables jointly by NBS and the USSR Academy of Sciences Thermocenter, Moscow. The scope has been established and preliminary evaluations have been made on properties of the element, oxides, chlorides, sulfides and aqueous ions. Data bases are being exchanged. Ultimately, the work will treat the element, oxide, halides, sulfides, sulfates, carbonates and silicates. These are the "basic" compounds upon which the thermochemistry of all other iron compounds and systems rest. The project also includes thermal functions for all compounds, and several high temperature systems (Fe-O , Fe-S , Fe-C and FeO-SiO_2) to be done in other laboratories.

The second is an evaluation of the thermochemistry of compounds of strontium that is related to the problem of storage of nuclear wastes. This is being done as part of a larger project sponsored by the OECD Nuclear Energy Agency. The NBS role in this work also includes assuring that the results are compatible with the current evaluations of data being made for CODATA.

B. Organic Thermochemistry
(E.S. Domalski, T. L. Jobe, Jr. with E. Hearing)

Two projects treat very different aspects of organic thermochemistry: prediction of properties of pure compounds and compilation of data on reusable biomass and industrial products.

1. Estimation Procedures

"Nearest neighbor group contributions" have been developed for hydrocarbons in condensed phases. The contributions, originally developed by Benson, have also been refined for the gas phase. These group values can be used to calculate enthalpies of formation, heat capacities and entropies at 298.15 K. Tests show that the agreement between experimental and predicted to be within 4 kJ/mole for the enthalpy of formation in condensed phases and 1 J/mol K for entropy in condensed phases. A manuscript is in preparation which will be sent to J. Phys. Chem. Reference Data.

2. Biomass

Thermodynamic data on material relevant to biomass utilization have been compiled. These include heat capacities, enthalpies of combustion, and some density data. This compilation extends earlier NBS work on incineration and waste recovery. The entire set will be published in 1986 jointly with the Solar Energy Research Institute.

C. Biochemical Thermochemistry
(D. Smith-Magowan)

Gibbs energies of formation for 22 species that are metabolized by the Krebs (or TCA) cycle were evaluated from experimental measurements of equilibrium constants for 30 enzymatic reactions and Gibbs energy of formations for 6 species calculated from enthalpies of combustion and Third law entropies.

The network formed by these reactions was fitted by the CATCH least squares programs to obtain the best internally consistent set of Gibbs formation energy values (at 298.15 K, 1 atm pressure and 0.1m ionic strength) for the 22 species comprising the network. The standard deviation of the residuals for the reactions was <0.5 kJ while the 95% confidence intervals for the resultant formation energies were ~1-2 kJ. This is a collaborative project with S.L. Miller, U. Calif., San Diego.

To our knowledge this is the first network treatment of the data. The values obtained represent a marked refinement over values compiled by Burton and Krebs, Wilhoit, Long and Johnson. A schematic diagram of the network is shown in Figure 2. New NBS measurements (Goldberg, Gajewski, Tewari, Steckler) on the fumarase to aspartase conversion equilibrium are significantly more consistent with the values predicted by the network solution than are earlier measurements on this conversion.

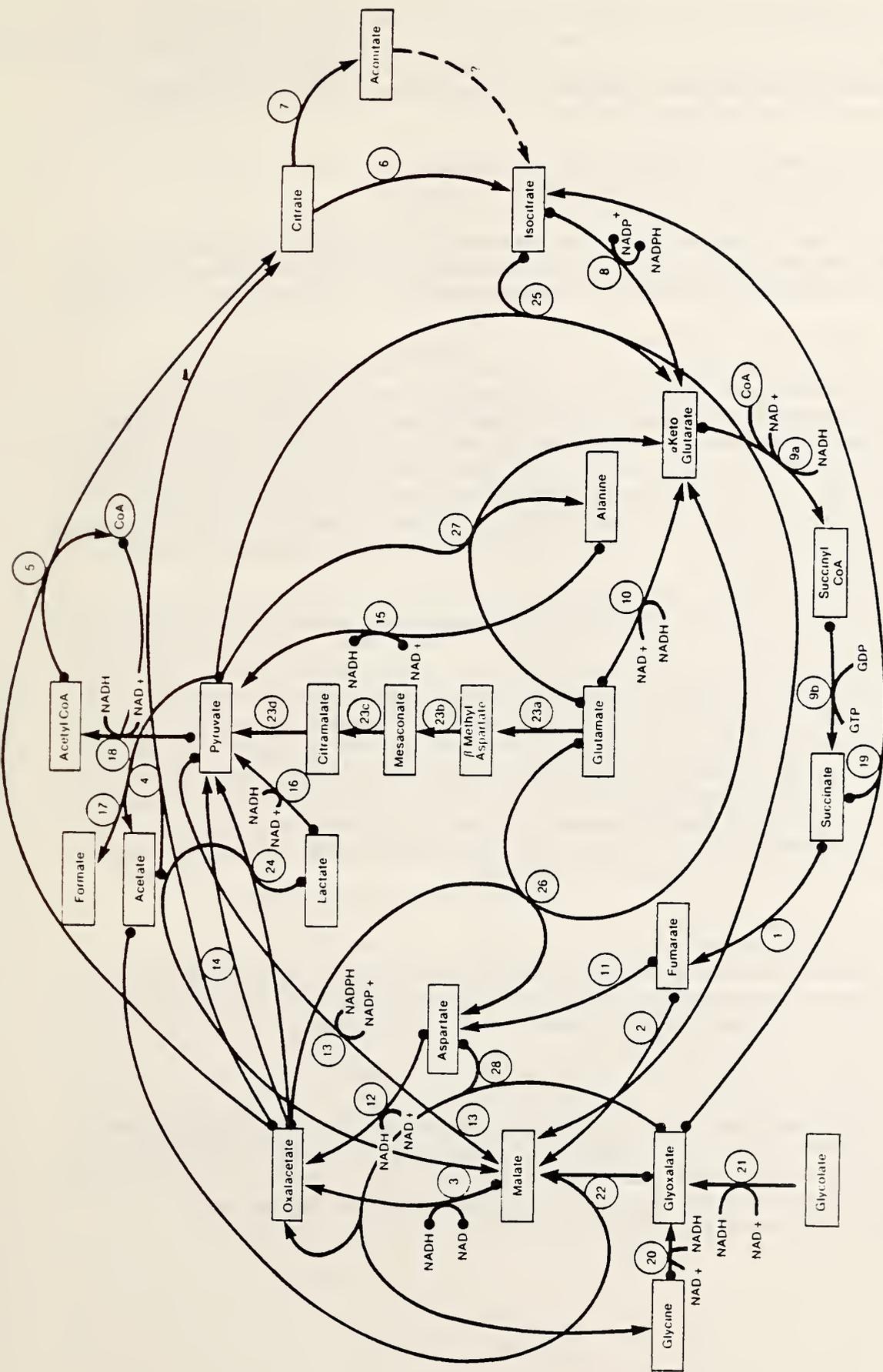


Fig. 2. Expanded Krebs cycle thermodynamic network: Each arrow represents a measured equilibrium constant. The circled numbers refer to the particular process as referenced in the paper to be published.

The importance of the Krebs cycle in the biological production of energy and its connection with many other metabolic and synthetic pathways ensures a broad-based constituency, among researchers concerned with many aspects of enzyme activity, that will benefit from this study and the continued application of the network analysis method.

D. Thermodynamics of Electrolyte Solutions
(D. Smith-Magowan, V. B. Parker, D. Garvin)

The thrust of the electrolyte data evaluation work has been to correlate properties in the T, P, x surface in a general manner. Calcium chloride has been the specific example studied.

1. Heat capacities for CaCl_2 as a Function of T and X

An evaluation has been made of the heat capacity of calcium chloride solutions as a function of temperature and composition. A new numerical algorithm has been used that was developed at the University of Delaware (and is described below). The correlation covers the temperature range 273-403 K and 0-11 molal, and is believed to be a more accurate representation of the data than those presented recently by Anathswamy and Atkinson and by Staples. A larger data set has been used than those used by the other authors.

2. Activity Coefficients and Enthalpies for CaCl_2 as a Function of T and X

A self consistent set of activity coefficients, excess enthalpies and excess heat capacities has been prepared for calcium chloride solutions, 298.15-373.15 K, 0-11 molal. These are based on the heat capacity correlation, previously evaluated activity coefficients and a new correlation of enthalpies of dilution. This work is being published as part of the CODATA Thermodynamic Tables. This work is believed to be the most self-consistent treatment of these properties throughout the given temperature and composition ranges.

3. Solubilities

Solubility data for calcium chloride solutions have been evaluated and recommendations made for the temperature range 223-530 K. These data also are being published in the CODATA Tables.

4. Sulfur Dioxide

"Thermodynamics of Solution of $\text{SO}_2(\text{g})$ in Water and Aqueous Sulfur Dioxide Solutions", by R.N. Goldberg and V.B. Parker is scheduled for publication in J. Res. NBS. This updates work reported previously and include consideration of unpublished measurements by Hepler and Dobrogowska. The work was supported by NBS OSRD, DoE and DIPPR.

E. Development of Methods for the Correlation of Properties of Solutions
(D. Smith-Magowan)

Methods have been developed for testing both strong and weak electrolytes.

1. Spline Procedures for the (T,P,X) Surface.

The algorithm developed at the University of Delaware for fitting C_p , and applied to data on calcium chloride solutions provides a spline fit as a function of temperature and composition. This gives a model independent numerical representation of the data. It appears to reproduce the data very well.

A major extension has been made of this algorithm to permit spline fitting of a mixed set of thermodynamic data (heat capacities, enthalpies, activities and PVT data) in terms of the independent variables T, P and composition. Tests of this extended algorithm against measurements for calcium chloride will be performed as soon as data collection is completed. This testing should start by the close of FY 1985.

2. Treatment of Weak Electrolytes

The article "An Equilibrium Model for the Calculation of Activity and Osmotic Coefficients in Aqueous Solutions", by R. N. Goldberg was published in J. Res. NBS, 89, pp 252-263 (1984). The model provides the capability to calculate activity and osmotic coefficients of the constituents of multicomponent mixtures in which multiple equilibria are taking place.

F. Data Base Development--General
(V.B. Parker, and with R.L. Nuttall, R.H. Schumm)

A continuing thrust is the preparation of numerical data bases for use in evaluations and to document past work.

1. Data Bases Developed at NBS

Five numerical data bases have been completed. Two document parts of the "NBS Tables of Chemical Thermodynamic Properties", and cover compounds of rubidium and lithium. One covers sulfur, its hydrides, oxides and oxyacids and is part of a project to develop data bases for use in flue gas cleanup studies for coal fired power plants. The fourth is based on the compilation of data relevant to biomass conversion. The fifth is a detailed listing of some 550 measurements required to define the thermochemical properties of common aqueous ions. It is being published as part of the "CODATA Key Values for Thermodynamics". (D. Neumann, D. Bickham, with J.B. Pedley)

2. Data Bases Contributed by Others

Four numerical data bases have been received as parts of collaborative programs. One hundred tables of thermal functions and a thermochemical data base on iron compounds have been obtained from the USSR Thermocenter. A thermochemical data base of measurements on iron, cobalt and nickel chlorides, together with thermal functions has been obtained from Dr. J.B. Pedley, University of Sussex. All of these are being used in current evaluations of data for CODATA.

The fourth is a file of evaluated data for enthalpies of formation for 3000 organic compounds from the University of Sussex data base plus enthalpies of formation for selected organo-phosphorus compounds evaluated at NBS.

G. Data Base Development -- Properties of Electrolyte Solutions (D. Smith-Magowan, R.N. Goldberg, V.B. Parker, R.L. Nuttall, J.L. Manley, D.K. Steckler)

Data bases and bibliographies have been prepared. The data base has been provided in magnetic tape format together with appropriate software.

1. Activity Coefficient Prediction Program

A data base of the activity coefficients of about 350 electrolytes was published on magnetic tape for distribution by OSRD. The companion documentation was published as NBS-Technical Note 1206 "GAMPHI-A Database of Activity and Osmotic Coefficients for Aqueous Electrolyte Solutions" by R. N. Goldberg, J. L. Manley and R. L. Nuttall. The program was structured to provide both interactive recall of values for desired compounds at specified concentrations and direct transfer of values to user programs via supplied subroutines.

2. Bibliographies of Industrial Interest

"A Bibliography of sources of Thermodynamic Data for the Systems: $\text{CO}_2+\text{NH}_3+\text{H}_2\text{O}$, $\text{CO}_2+\text{H}_2\text{S}+\text{H}_2\text{O}$, $\text{H}_2\text{S}+\text{NH}_3+\text{H}_2\text{O}$, and $\text{CO}_2+\text{NH}_3+\text{H}_2\text{S}+\text{H}_2\text{O}$ " by R. N. Goldberg, and D.K. Steckler was issued as NBS Spec. Publ. 699. This work was supported in part by DIPPR whose concern focusses on the chemical processing of such mixtures as they occur in wastewater streams. Other bibliographies that were submitted to DIPPR at the end of FY 85 will soon be available for issuance as NBS documents. During the past year additional material has been identified that will necessitate minor revision of the monographs prior to publication.

H. Accessions, Information, and Support
(D. Cockrell, T.L. Jobe, P. Fagan, C. Jackson, with E. Hearing,
W.H. Evans and N. Young)

These are ongoing activities that make possible the systematic evaluation of data. During the year 3500 articles from the current literature have been located, abstracted, and entered in our index to thermodynamic measurements. This work also is the basis for the Inorganic Substances section of volume 28 of the Bulletin of Chemical Thermodynamics. Emphasis in the current year has been to streamline day-to-day operations including making more use of automated retrieval from Chemical Abstracts on Line. In addition, the use of automated searches and the production of reports from our files has been significantly expanded and simplified.

I. Automation Activities
(D. Bickham, P. Fagan, D. Neumann)

Four data centers share the use of an HP-1000 mini-computer via terminals and interfaced personal computers. Principal uses of the mini-computer are word processing and data manipulation. Calculations and graphics are a small but growing fraction of the work load. Individual researchers reduce and model data. Users are supported by the automation group of the Chemical Thermodynamics Data Center which is responsible for system maintenance and development.

1. Computer Upgrade

In FY1985 the mini-computer system received a major upgrade with a faster CPU, larger memory, and a more flexible operating system. Software for graphics, data management, and communications were purchased and numerical analysis packages were down-loaded from the NBS central facility. Personal computer software packages, such as LOTUS 1-2-3 and WORDSTAR, have been put into use and are being integrated with applications running on the mini-computer.

2. Data Communications

Transfers of data and text between personal computers, the NBS main frame, the NBS typesetting system, the secretarial workstations, and the data center's mini-computer are now possible. In addition, computer-to-computer communications with cooperating researchers outside NBS, have been enhanced and simplified. Transfers of data to NBS are now being made from JANAF (Midland, MI), ENSEEG (Grenoble, France), AERE (Harwell, UK), and Thermodynamic Research Center (College Station, Texas) Transfer on tape remains the method used for data from the Academy of Sciences Thermocenter (Moscow, USSR).

3. Cooperative Program with the Univ. Sussex.
(with J.B Pedley, A. Pedley)

In a joint effort during the summer of FY85 with J. B. Pedley, Univ. of Sussex, UK., the data center has imported several of his programs, converted them for use on the HP-1000, and begun to integrate them with other modules. These programs consist of the following:

(a) Thermochemical calculations. These consist of a set of programs for the management, adjustment, and prediction of thermodynamic data for chemical and physical processes. The system provides for storage of raw data, reduction of equilibrium data, comparison of measurements with previous selections, and calculation of tables of thermal functions.

(b) Organic Search and Retrieval System. This program is a data storage and retrieval system based on a new notation for organic functional groups. With this system thermodynamic data, at present enthalpies of formation, can be retrieved for compounds having common substructures. The associated data base is the entire Sussex Thermochemistry file.

(c) Prediction of Enthalpy of Formation for Organic Species. This set of programs predicts enthalpies of formation of organic substances. It is based on a group contribution method that allows some next-nearest-neighbor interactions. An effort is underway to extend this work to heats of vaporization, heat capacities, and entropies, and to compare its performance with the prediction scheme developed by E.S. Domalski at NBS.

4. Information Processing

A number of efforts have been made this year to streamline our day to day operations and to enhance access to our data base by evaluators. These efforts consist of:

(a) A bibliographic retrieval system with printed and on-line documentation which is almost complete. It is under test currently with 40,000 references from CTDC's pre-1969 bibliography (with W.H. Evans).

(b) New programs for processing abstracts which have been completed, tested and are now in use. With these programs the collection of abstracts from 1970 to 1985 have been prepared for loading to the CTDC data base. In addition, these programs have processed the inorganic contribution to volume 27 and 28 of the Bulletin of Chemical Thermodynamics and have also been used to reformat the organic contribution from Texas A&M to volume 27 of BCT.

(c) The automation of the storage, retrieval, and printing of tabular thermal function data with a report generator. This system was used to produce chapters in the "CODATA Thermodynamic Tables" and the "CODATA Key Values for Thermodynamics". It is expected that in the next year these

programs will be integrated with the programs for management of chemical reaction data obtained from U. of Sussex this year (see above) (with R.J. Cvetanovic).

(d) A further success has been the coordinated planning, and implementation of a chemical species and chemical reaction retrieval system. This joint effort with the Chemical Kinetics and Surface Science Divisions has proceeded to a point where plans are firm and programs for storage and retrieval have been written and are being tested. In its final form this system will permit on-line access (at NBS) to evaluated kinetic and thermodynamic data using a uniform system of programs and utilities based on shared substance, reaction, and bibliographic data bases.

J. Plans for FY 86 include

1. Thermodynamic Data Evaluation.

Recommended values will be developed for thermochemical properties of selected compounds of iron (with possible extension to cobalt and nickel), selected compounds of strontium, and for nitrogen-oxygen-sulfur compounds. These projects are, respectively, in support of the CODATA Thermodynamic Tables, The NEA Nuclear Waste Study, and the DoE Flue Gas SO_x-NO_x Removal Program.

An analysis will be made of data on equilibria in biochemical cycles closely related to the Krebs cycle, as part of the NBS Biotechnology Program.

A major new project will be the preparation of tables of thermal functions for use in science and industry. (This will be done by merger of the JANAF Tables into the NBS thermodynamic data activity.)

A new procedure for analyzing thermophysical and volumetric properties in terms of a (T, density, composition) surface for solutions of strong electrolytes and their mixtures will be tested and applied to CaCl₂-H₂O. This is part of a joint project with the Univ. of Delaware.

Estimation of enthalpies of formation of organic compounds will be extended to organophosphorus compounds. This is part of a joint project with the Univ. of Sussex.

2. Data Base Development

Catalogs will be prepared of measurements on thermodynamic properties of compounds of iron, and strontium, and of N-O-S compounds.

Previously prepared catalogs of measurements will be prepared for publication.

Current articles on thermodynamics and molecular properties (about 3500) will be selected, abstracted and used in the NBS Thermodynamic Index and the Bulletin of Chemical Thermodynamics.

A heat capacity, enthalpy and molecular properties data base will be developed from the joint holdings of NBS, JANAF and Univ. of Sussex.

3. Thermodynamics of Aqueous Electrolyte Solutions

The algorithm for fitting properties of electrolyte solutions versus T, P, and x will be tested against data collected for CaCl_2 . The results of this study will be prepared for publication. Data for KCl solutions are being collected since this is the next candidate for treatment by this method.

A proposal to DIPPR for the development of a microcomputer based interactive database system for the thermodynamic properties of electrolytes as functions of temperature and pressure has been accepted and support is expected to begin with calendar year 86. The proposal calls for approximately 6 persons months of effort per year for the next three years. Objectives for the first year include supplementing the existing Gibbs energy collection and developing software modules for calculating engineering quantities, estimating methods and diagnostic testing for complexing and ion association.

4. Biothermochemical Equilibria.

The network analysis used for the Krebs cycle will be applied to additional cycles that are connected to the Krebs cycle. The exact choices have not been made but candidates included the glycolytic pathway, ATP-citrate lyase sequence, catalyzed amino acid syntheses and others.

5. Automation Activities

The emphasis in FY86 will be to place the joint Kinetics, Ion-Energetics, Surface Science, Chemical Thermodynamics data base system into full operation. This will be an on-line system, screen oriented, if possible, with a common chemical dictionary and bibliographic protocol but separate kinetics and thermodynamics data files.

Calculational programs for thermodynamic properties will be integrated with the existing NBS data base. Existing predictive systems such as that from Sussex will also be incorporated and further documented to allow greater access and use.

The management of computer operations for the several data centers using the mini-computer will continue with programming services, selection of new software and hardware, and integration of micro-and mini-computer capabilities. An effort will be made to encourage word-processing and small calculations on the micro's and to encourage shared uses such as data bases, complex programs, and graphics on the mini-computer.

5. PUBLICATIONS

(a) Publications of Past Year

- Abramowitz, S., "Biotechnology and Bioseparations", Proceedings of the National Science Foundation Workshop, Thermodynamics Needs for the Decade Ahead: Theory and Experiment. October 28-29, 1983, S. Sandler, Ed.; Vol.1, 55-66 (1985) and Vol.2.
- Ammon, H.L., Murphy, K.C., Chandrasekhar K. and Wlodawer, A., "Preliminary Crystallographic Study of an L-Asparaginase from *Vibrio Succinogens*", J. Mol. Biol., 184, 179 (1985).
- Borah, B., Chen, C., Egan, W., Miller, M., Wlodawer, A. and Cohen, J., "Nuclear Magnetic Resonance and Neutron Diffraction Studies of the Complex of RNase A with Uridine Vanadate, a Transition-State Analog", Biochemistry, 24, 2058 (1985).
- Buckley, T.J., Sieck, L.W., Metz, R. and Lias, S.G., "Consecutive Ion-Molecule Condensation Reactions and Photodissociation Mechanisms of Condensation Ions in Polyacetylenic Compounds", Int. J. Mass. Spectrometry and Ion Processes, 65, 181 (1985).
- Busenberg, E., Plummer L.N., Parker, V.B., "The Solubility of Strontianite (SrCO_3) in CO_2 and H_2O Solutions Between 2 and 92 °C, the Association Constants of SrHCO_3 (aq) and SrCO_3 (aq) Between 5 and 80 °C and an Evaluation of the Thermodynamic Properties of Sr^{2+} (aq) and SrCO_3 (cr) at 25 °C and 1 Atmosphere", Acta Geochimica 48, 2021 (1984).
- Churney, K.L., Ledford, Jr., A.E., Bruce, S.S. and Domalski, E.S., "Chlorine Content of Municipal Solid Waste from Baltimore County, MD and Brooklyn, NY", NBSIR 85-3213, April (1985).
- Colbert, J.C. and Kirklin, D.R., "Determination of Sulfur, Calorific Value, and Ash Content in NBS Coals Using ASTM Procedures D2015, D3180, D3177, D3173, and D3174", Chapter III of NBS Special Publication 260-94, T.E. Gills, editor; "Standard Reference Materials: Methods and Procedures Used at the National Bureau of Standards to Certify Sulfur in Coal SRM's for Sulfur Content, Calorific Value, and Ash Content", December (1984).
- Colbert, J.C., "Certificate of Analysis, Standard Reference Material 1657, Synthetic Refuse Derived Fuel Combustion Calorimetric Standard", February (1985).
- Domalski, E.S., Churney, K.L., Ledford, Jr., A.E., Colbert, J.C., Bruce, S.S., Buckley, T.J., Paule, R.C. and Reilly, M.L., "Determining the Calorific Value of Municipal Solid Waste: Experimental Results from a 2.5 Kilogram-Capacity Flow Calorimeter", Proceedings of Energy from Municipal Waste Research Workshop held in Kissimmee, Florida, February 22-24, 1984, 29-47, (ANL/CNSV-TM-144).
- Gajewski, E., "Radiation-Induced Products of Peptides and Their Enzymatic Digestibility", Dissertation Abstracts International, 44, 3813-B (1984).

- Gajewski, E., Dizdaroglu, M., Krutzsch, H.C. and Simic, M.G., "OH Radical-Induced Dimerization and Racemization of Methionine in Peptides", *Int. J. Radiat. Biol.*, 46, 47 (1984).
- Garvin, D., Domalski, E.S., Wilhoit, R.C., Somayajulu, G.R. and Marsh, K.N., "Heating Values of Components of Natural Gas", *Proc. Symp. "Natural Gas Energy Measurements"*, August 26-28, Chicago, Ill., (1985).
- Garvin, D., Goldberg, R.N. and Staples, B.R., "Evaluated Data and Data Bases: Chemical Thermodynamics in the Steam Power Cycle", *Proceedings of the Workshop in Steam Power Cycles Data Requirements*, H. White and O. Jonas, Editors, February 8-9, 1983, NBSIR 85-3205, July (1985).
- Goldberg, R.N., "Compiled Thermodynamic Data Sources for Aqueous and Biochemical Systems: An Annotated Bibliography (1930 to 1983)", NBS Special Publication 685, U.S. Government Printing Office, Washington, DC, (1984).
- Goldberg, R.N., Manley, J.L. and Nuttall, R.L., "GAMPHI - A Database of Activity and Osmotic Coefficients for Aqueous Electrolyte Solutions", NBS Technical Note 1206, U.S. Government Printing Office, Washington, DC, (1985).
- Goldberg, R.N. and Steckler, D.S., "A Bibliography of Sources of Thermodynamic Data for the Systems: $\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O}$, $\text{CO}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$, $\text{H}_2\text{S} + \text{NH}_3 + \text{H}_2\text{O}$, and $\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{S} + \text{H}_2\text{O}$ ", NBS Special Publication, 69, U.S. Government Printing Office, Washington, DC, (1985).
- Johnson, W.H., "Certificate of Analysis, Standard Reference Material 2154, Nicotinic Acid Combustion Calorimetric Standard", 1985.
- Johnson, W.H., "Certificate of Analysis, Standard Reference Material 2152, Urea, Combustion Calorimetric Standard", 1985.
- Kirchhoff, W.H., "A National Program of Measurement Services and Standards for Biotechnology at the National Bureau of Standards", National Bureau of Standards, Planning Report 22, March (1985).
- Kirklin, D.R., Decker, P.H. and Domalski, E.S., "Characterization of Refuse-Derived Fuel at Various Stages of Processing", *Resources and Conservation* 11, 255 (1985).
- Kirklin, D.R. and Domalski, E.S., "Certificate of Analysis, Standard Reference Material 1656, Thianthrene, Combustion Calorimetric Standard", January (1985).
- Owens, J.W., DeVoe, H., Buckley, T.J. and Wasik, S.P., "An Automated Coupled-Column Chromatography System for Measuring Aqueous Solubilities of Hydrophobic Solutes", *J. Research NBS* 90, 41 (1985).
- Simic, M.G., Gajewski, E. and Dizdaroglu, M., "Kinetics and Mechanisms of Hydroxyl Radical-Induced Crosslinks Between Phenylalanine Peptides", *Radiat. Phys. Chem.* 24, 465 (1985).

- Smith-Magowan, D., "Evaluation of the Applicability of Colloid Studies to Cobalt-60 Deposition in LWRs", NP-3773 Electric Power Research Institute, Palo Alto, CA, November (1984).
- Smith-Magowan, D., "The Impact of Colloidal Chemistry on Radioactivity Transport in Nuclear Power Plants", NP-4032 Electric Power Research Institute, Palo Alto, CA, May (1985).
- Steitz, T.A. and Weber, I.T., "Structure of Catabolite Gene Activator Protein", In Biological Macromolecules and Assemblies, Vol.2: Nucleic Acids and Interactive Protein (F. Journak and A. McPherson, editors), John Wiley and Sons, Inc., New York, 289 (1985).
- Tewari, Y.B. and Goldberg, R.N., "A Note on the Thermodynamics of the Conversion of Aqueous Glucose to Fructose", Applied Biochemistry Biotechnology, 11, 17 (1985).
- Tsang, W., Macek, A., Domalski, E.S., Walker, J.A., Charagundle, S.R., Colbert, J.C., Kirklin, D.R., Ledford, Jr., A.E., Decker, P.H. and Ryan, R.V., "Combustion Characteristics of Refuse Derived Fuel", NBSIR 83-1343, October (1984).
- Wasik, S.P., Schwarz, F.P., Tewari, Y.B., Miller, M.M. and Purnell, J.H., "A Head-Space Method for Measuring Activity Coefficients, Partition Coefficients and Solubilities of Hydrocarbons in Aqueous Solutions", NBS J. Res. 89, 273 (1984).
- Weber, I.T. and Steitz, T.A., "A Model for the Non-Specific Binding of Catabolite Gene Activator Protein to DNA", Nucleic Acids Res. 12, 8475 (1984).
- Weber, I.T. and Steitz, T.A., "The Crystallization of rec A Protein from Proteus Mirabilis", NBSIR 85-175, September (1985).
- Wlodawer, A., "Structure of Bovine Pancreatic Ribonuclease", in Biological Macromolecules and Assemblies, Vol.II: Nucleic Acids and Interactive Proteins, A. McPherson and F. Journak, eds., John Wiley: New York, 393-439 (1984).
- Wlodawer, A. and Sjolin, L., "Application of Joint Neutron and X-ray Refinement to the Investigation of the Structure of Ribonuclease A at 2.0 A Resolution", in Neutrons in Biology, B.P. Schoenborn, ed., Plenum Publishing Corporation, 349-364 (1984).
- Wlodawer, A., Walter, J., Huber, R. and Sjolin, L., "Structure of Bovine Pancreatic Trypsin Inhibitor: Results of Joint Neutron and X-ray Refinement of Crystal Form II", J. Mol. Biol., 180, 301 (1984).

(b) Publications in Progress

- Ditmars, D.A., "Drop Calorimetry above 300 K", McGraw-Hill/CINDAS Data Series on Material Properties, Chap. 13, Compendium of Thermophysical Property Measurement Methods, Vol. I, Plenum Publishing Corporation, 1985, (in press).
- Ditmars, D.A., Plint, C.A. and Shukla, R.C., "Aluminum (I): Measurement of the Relative Enthalpy from 273 to 929 K; Derivation of Thermodynamic Functions for Al(s) from 0 K to Its Melting Point", Int. J. Thermophysics, 1985, (in press).
- Gajewski, E., Goldberg, R.N. and Steckler, D.K., "Thermodynamics of the Conversion of Fumarate to L(-)malate", Biophys. Chem., (in press).
- Garvin, D., Staples, B.R. and Jobe, Jr., T.L., "A Bibliography on the Equilibria in the $\text{CuCl}_2\text{-H}_2\text{O}$ System", Handbook of Aqueous Thermodynamics, Design Institute for Physical Property Data, (DIPPR), (submitted).
- Goldberg, R.N., Gajewski, E., Steckler D.K. and Tewari, Y.B., "Thermodynamics of the Conversion of Aqueous L-aspartic Acid to Fumaric Acid and Ammonia", (submitted).
- Goldberg, R.N. and Parker, V.B., "Thermodynamics of Solution of $\text{SO}_2(\text{g})$ in Water and of Aqueous Sulfur Dioxide Solutions", J. Res. NBS, (in press).
- Jobe, T.L. and Goldberg, R.N., "A Bibliography of Sources of Thermodynamic Data for Aqueous Phosphoric Acid Solutions", Handbook of Aqueous Thermodynamics, Design Institute for Physical Property Data, (DIPPR), (submitted).
- Jobe, T.L. and Goldberg, R.N., "A Bibliography of Sources of Thermodynamic Data for Aqueous Zinc Chloride Solutions", Handbook of Aqueous Thermodynamics, Design Institute for Physical Property Data, (DIPPR), (submitted).
- Johnson, W.H. and Prosen, E.J., "Determination of Enthalpies of Combustion and Formation of Substituted Triazines in an Adiabatic Bomb Calorimeter", J. Res. NBS, (in press).
- Karpas, Z., Stevens, W.J., Buckley, T.J. and Metz, R., "The Proton Affinity and Gas Phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate and Methyl Thiocyanate", J. Phys. Chem., (in press).
- Kirchhoff, W.H. and Levin, I.W., "Description of the Thermotropic Behavior of Membrane Bilayers in Terms of Raman Spectral Parameters: A Two-State Model", (submitted).
- Miller, M.M., Wasik, S.P., Guang, G.L., Shiu, W.Y. and MacKay, D., "Relationships Between Octanol-Water Partition Coefficients, Aqueous Solubility and Bioconcentration Factors", (submitted).

- Neumann, D.B., "Data Base Management Systems, Part I. A Quick Overview", Proceedings of "Training Course in Accessibility and Dissemination of Non-Bibliographic Data in Science and Technology", October 1983, CODATA, (in press).
- Neumann, D.B., "Data Base Management Systems, Part II. An Application to Scientific Technical Data and its Associated Bibliographic Data", Proceedings of "Training Course in Accessibility and Dissemination of Non-Bibliographic Data in Science and Technology", October 1983, CODATA, (in press).
- Owens, J.W., Wasik, S.P. and DeVoe, H., "Aqueous Solubilities and Enthalpies of Solution of n-Alkylbenzenes", J. Chem. Eng. Data, (in press).
- Savage, H. and Wlodawer, A., "Determination of Water Structure Around Biomolecules Using X-ray and Neutron Diffraction Methods", Methods in Enzymology (Biomembranes), (in press).
- Schwarz, F.P., "Positive Charge Transfer in the UV Photolysis and β Radiolysis of Trans-Decalin Solutions", J. Phys. Chem., (in press).
- Shukla, R.C., Plint, C.A. and Ditmars, D.A., "Aluminum(II): Derivation of C_{V0} from C_p and Comparison to C_{V0} Calculated from Anharmonic Models", Int. J. Thermophysics, (in press).
- Tewari, Y.B. and Goldberg, R.N., "An Investigation of the Equilibria Between Aqueous Ribose, Ribulose and Arabinose", Biophys. Chem. (in press).
- Tewari, Y.B., Steckler, D.S. and Goldberg, R.N., "Thermodynamics of the Conversion of Aqueous Xylose to Xylulose", Biophys. Chem. (in press).
- Wlodawer, A., "A Facility for Data Collection and Processing at the National Bureau of Standards Reactor", in Methods in Enzymology, H.W. Wyckoff, C.H.W. Hirs, and S.N. Timasheff, eds., Academic Press: New York, (in press).
- Wlodawer, A., Borkakoti, N., Moss, D.S. and Hawkin, B., "Comparison of Two Independently Refined Models of Ribonuclease A", Acta Cryst., (in press).
- Zielinski, W.L., Miller, M.M., Ulma, G. and Wasik, S.P., "GLC Separation of Polychlorinated Biphenyl Isomers Between a Nematic Liquid Phase and a Non-Polar Base", (submitted).

6. TALKS

- Abramowitz, S., "NBS' Proposed Biotechnology Program", Center for Chemical Engineering, NBS, Boulder, CO, December 8, 1984.
- Abramowitz, S., "NBS' Program in Support of AFOSR's Spacecraft Survivability Program", Obscuration and Aerosol Research Chemical and Research Development Center, Aberdeen, MD, June 19, 1985.
- Buckley, T., "Interfacing of Heat Conduction Microcalorimeters to a Microcomputer", IUPAC Thermodynamics Conference, Hamilton, Ontario, Canada, August 1984.
- Buckley, T., "Consecutive Ion-Molecule Reactions in Diacetylene and Related Systems", Sixth East Coast Ion Cyclotron Resonance and Ion Molecule Chemistry Symposium, September 22, 1984.
- Buckley, T., "The Gas Phase Ion Chemistry and Proton Affinity of Methyl Isocyanate, Methyl Isothiocyanate and Methyl Thiocyanate", American Society for Mass Spectrometry, San Diego, California, May 27, 1985.
- Churney, K.L., "Recent Developments in Large Sample Flow Calorimetry", 40th Annual Calorimetry Conference, Pacific Grove, California, August 29, 1985.
- Colbert, J.C., "Enthalpy of Combustion of 2-Deoxy-D-Ribose", 40th Annual Calorimetry Conference, Pacific Grove, California, August 27, 1985.
- Ditmars, D.A., "Measured Heat Capacity of fcc Strontium", 9th Annual Symposium on Thermophysical Properties, University of Colorado, Boulder, Colorado, June 1985.
- Ditmars, D.A., "Heat Capacity of fcc and bcc Calcium; Derived Thermodynamic Functions", 40th Annual Calorimetry Conference, Pacific Grove, California, August 26, 1985.
- Domalski, E.S., "Estimation Methods and Combustion Calorimetry for Organic Phosphorus Compounds", 1984 Scientific Conference on Chemical Defense Research, U.S. Department of the Army, CRDC, Aberdeen Proving Ground, Maryland, November 16, 1984.
- Domalski, E.S., "The Chlorine Content of Municipal Solid Waste", ASME Dioxin Committee, United Engineering Center, New York, NY, January 23, 1985.
- Domalski, E.S., "Materials and Energy Balances for Chlorine during MSW Combustion", ASTM Committee E-38 on Resource Recovery Subcommittee E-38.01 on Energy, Bear Mountain Inn, Bear Mountain, New York, March 25, 1985.
- Domalski, E.S., "Materials and Energy Balances for Chlorine during MSW Combustion", ASME Research Committee on Industrial and Municipal Wastes, Bear Mountain Inn, Bear Mountain, New York, March 26, 1985.

- Domalski, E.S., "Thermodynamic Data Evaluation and Estimation for Organic Phosphorus Compounds", 40th Annual Calorimetry Conference, Pacific Grove, California, August 29, 1985.
- Domalski, E.S., "Monitoring the Fate of Chlorine from MSW Sampling through Combustion", 5th International Symposium of Chlorinated Dioxins and Related Compounds, University of Bayreuth, Bayreuth, West Germany, September 17, 1985.
- Domalski, E.S., "The Chlorine Content of MSW", Warren Spring Laboratory, Stevenage, United Kingdom, September 24, 1985.
- Domalski, E.S., "Recent Studies in the NBS Large Sample Flow Calorimeter using Oxygen/Nitrogen Mixtures", Warren Spring Laboratory, Stevenage, United Kingdom, September 24, 1985.
- Gajewski, E., "Thermodynamics of the Conversion of Fumarate to L(-)malate", 29th Meeting of the Biophysical Society, Baltimore, Maryland, February 27, 1985.
- Gajewski, E., "Thermodynamics of Fumarase and L-aspartase Reactions", Biotechnology Seminar, National Bureau of Standards, Gaithersburg, Maryland, September 19, 1985.
- Garvin, D., "Heating Values of Components of Natural Gas", Institute of Gas Technology Symposium, Chicago, Illinois, August 26, 1985.
- Garvin, D., "Comprehensive Consistent Thermodynamic Tables", International Meeting on Phase Equilibrium Data, Paris, France, September 8, 1985.
- Goldberg, R.N., "DIPPR Project 811 at the National Bureau of Standards", Presentation to DIPPR Panel, AIChE Meeting, San Francisco, California, November 1984.
- Goldberg, R.N., "A Computerized Electrolyte Data Base", Conference on Electrolyte Solutions in Science and Engineering; Thermodynamics Division, National Bureau of Standards, Gaithersburg, Maryland, June 11, 1985.
- Kirchhoff, W.H., "Modeling Phase Transitions in Lipid Bilayers: Fitting Sigmoidal Curves Without Sufficient Data", Statistical Engineering Division Seminar Series, National Bureau of Standards, Gaithersburg, Maryland, October 2, 1984.
- Kirklin, D.R., "Combustion Bomb Calorimetry of Key Organic Phosphorous Compounds", 40th Annual Calorimetry Conference, Pacific Grove, California, August 29, 1985.
- Neumann, D.B., "The New RTE-A Operating System for the HP-1000 Computer", Chemical Thermodynamics and Chemical Kinetics Division Seminar, National Bureau of Standards, Gaithersburg, Maryland, February 24, 1985.

- Parker, V.B., "Thermodynamics of Solution of SO₂(g) in Water and of Aqueous Sulfur Dioxide Solution", Conference on Electrolyte Solutions in Science and Engineering, Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland, June 11, 1985.
- Smith-Magowan, D., "Electrolyte Data Center, Where Are You?", Conference on Electrolyte Solutions in Science and Engineering, Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland, June 11, 1985.
- Tewari, Y.B., "Thermodynamic Investigations of the Reactions Catalyzed by Glucose (xylose) Isomerase", Chemical Thermodynamics Division Seminar, National Bureau of Standards, Gaithersburg, Maryland, February 26, 1985.
- Tewari, Y.B., "Thermodynamic Investigations of the Reactions Catalyzed by Glucose (xylose) Isomerase", 7th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, Tennessee, May 15, 1985.
- Tewari, Y.B., "Thermodynamic Investigations of the Equilibria Between Aqueous Ribose, Ribulose and Arabinose", 40th Annual Calorimetry Conference, Pacific Grove, California, August 29, 1985.
- Tewari, Y.B., "Thermodynamics of the Conversion of L-aspartate to Fumarate", 40th Annual Calorimetry Conference, Pacific Grove, California, August 29, 1985.
- Weber, I.T., "Structural Studies of Three Anti-tumor Amidohydrolases", American Crystallographic Association, Stanford California, August 19-23,, 1985.
- Weber, I.T., "The Analysis of Protein Structure from Crystallographic Data", Course on Protein Structure and Function, Les Diablerets, Switzerland, September 30 - October 3, 1985.
- Weber, I.T., "The Structure of Catabolite Gene Activator Protein and Its Complex with DNA", Course on Protein Structure and Function, Les Diablerets, Switzerland, September 30 - October 3, 1985.
- Wlodawer, A., "Macromolecular Diffractometer using a Position-sensitive Detector", Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania, November 9, 1984.
- Wlodawer, A., "Neutron Diffraction Studies of BPTI, RNase and Insulin", Argonne National Laboratory, Argonne, Illinois, November 28, 1984.
- Wlodawer, A., "Neutron Diffraction Studies of BPTI", University of Chicago, Chicago, Illinois, November 29, 1984.
- Wlodawer, A., "Neutron and X-ray Diffraction Studies of Proteins", George Mason University, Fairfax, VA, February 22, 1985.
- Wlodawer, A., "Protein Structure by Neutron and X-ray Diffraction", Staff Research Seminar, National Bureau of Standards, Gaithersburg, Maryland, March 21, 1985.

Wlodawer, A., "Neutron Diffraction Studies of Proteins", Northern Virginia Community College, Annandale, VA, May 24, 1985.

Wlodawer, A., "Determination of Protein Structure by Neutron Diffraction", University of Regensburg, West Germany, June 25, 1985.

Wlodawer, A., "Determination of Protein Structure by Neutron Diffraction", University of Uppsala, Sweden, July 5, 1985.

Wlodawer, A., "Joint Neutron and X-ray Structural Refinement of Porcine Insulin", ACA Summer Meeting, Stanford University, California, August 20, 1985.

Wlodawer, A., "Neutron Diffraction Studies of Proteins", University of California, San Francisco, California, August 23, 1985.

7. CHEMICAL THERMODYNAMICS DIVISION SEMINARS

* Breganza, L.F., Institut Laue-Langevin, Grenoble, France, "High Pressure Neutron Diffraction Studies of Biological Membranes", May 16, 1985.

* Calton, Gary J., Purification Engineering, Inc., Columbia, Maryland, "Industrial Use of Enzymes in the Production of Specialty Chemicals", March 14, 1985.

Chase, Malcolm W., Dow Chemical Company, Midland, Michigan, "Thermochemistry of the Alkaline Earth Metals and their Compounds - Data Evaluation, Theory and Experiment", July 15, 1985.

* Gajewski, Ewa, National Bureau of Standards, "Thermodynamics of Fumarase and L-aspartase Reactions", September 19, 1985.

* Gershon, Nahum, National Institute of Health, Bethesda, Maryland, "Three Dimensional Image Processing and Computer Graphics of Cytoplasmic Structures", May 17, 1985.

* Gilliland, Garry, Genex Corporation, Gaithersburg, Maryland, "The Crystallization of Biological Macromolecules", September 20, 1985.

* Lehmann, M.S., Institut Laue-Langevin, Grenoble, France, "Small-angle and Single-crystal Neutron Scattering Studies of Ethanol-lysozyme Interactions", November 2, 1984.

Lenz, Terry G., Chemical Engineering Department, Colorado State University, Fort Collins, Colorado, "Chemical Equilibria in Diels-Aldler Processes", August 5, 1985.

Orser, Donald, National Bureau of Standards, "An Algorithm for Producing Alloy Phase Diagrams", March 1985.

* Tewari, Yadu B., National Bureau of Standards, "Thermodynamic Investigations of the Reactions Catalyzed by Glucose (xylose) Isomerase", February 26, 1985.

* Thompson, Peter T., Swarthmore College, "Weak Forces in Chemistry and Their Role in Biological Systems", March 12, 1985.

* Tolbert, William R., The Monsanto Company, Saint Louis, Missouri, "Perfusion Culture Systems for Production of Mammalian Cell Biomolecules", January 23, 1985.

* Biotechnology Seminars

8. TECHNICAL AND PROFESSIONAL COMMITTEE
PARTICIPATION AND LEADERSHIP

Abramowitz, S.

ASTM Committee E-38 on Resource Recovery, Subcommittee E38.01 Energy

Churney, K.L.

ASTM Committee E-37 on Thermal Measurements

ASTM Committee on Hazard Potential of Chemicals, Subcommittee E-27.02 on Thermal Stability

ASTM Committee E-38 on Resource Recovery

Colbert, J.C.

ASTM Committee E-38 on Resource Recovery, Subcommittee E38.01 Energy
(Member)

Ditmars, D.A.

ASTM Committee E37.05 (Thermal Measurements/Thermophysical Properties)
Section I (Thermodynamics) Task Group 1.5 (Drop Calorimetry), 1.6
(Adiabatic Calorimetry)

Division Safety Officer

Standards Committee, U.S. Calorimetry Conference (Member)

Domalski, E.S.

ASTM Committee E-27 on Hazard Potential of Chemicals, Subcommittee
E-27.07 Computational Methods (Member)

ASME Research Committee for Industrial and Municipal Wastes (Member)

ASTM Committee E-38 on Resource Recovery, Subcommittee E-38.01 Energy
(Member)

Garvin, D.

CODATA Task Group on Chemical Thermodynamic Tables (Secretary)

ASTM Committee E-38 on Resource Recovery (Member)

ASTM Committee E-27 Hazard Potential of Chemicals (Member)

Goldberg, R.N.

Councilor, U.S. Calorimetry Conference

Kirchhoff, W.H.

ASTM Committee E-47 on Biological Effects and Environmental Fate
(Chairman)

ASTM Committee D-19 on Water (Member)

ASTM Coordinating Committee on Environmental Activities (Member)

ASTM Committee E-48 on Biotechnology (Member)

IUPAC Commission I.1. on Physicochemical Symbols, Terminology and Units
(Titular Member)

Kirklin, D.R.

ASTM Committee E-38 on Resource Recovery, Subcommittee E-38.01 on Energy
(Member) Subcommittee E-38.02 on Research (Member)

Director, U.S. Calorimetry Conference

Division Property Officer

Neumann, D.B.

Hewlett-Packard HP1000 International Users Group (Member)

Parker, V.B.

IAEA Committee on Chemical Thermodynamics of Actinide Elements and
Compounds (Consultant), Subcommittee IAEA.WG.01 Actinide Halide
Thermodynamics

CODATA Task Group on Chemical Thermodynamic Tables (Corresponding
Member)

Wlodawer, A.

Neutron Special Interest Group of the American Crystallographic
Association (Treasurer)

NIH Macromolecular Studies Program, Yale University (Member)

Conference on Protein Crystal Growth, Stanford University (Member)

9. PROFESSIONAL INTERACTIONS, CONSULTING
AND ADVISORY SERVICES

Abramowitz, S.

Collaboration with I.W. Levin, National Institute of Arthritis and Metabolic Disease, NIH, on vibrational analysis of small molecules and some biological species.

Formulation of cooperative research program on high temperature thermodynamics with AFOSR.

Interactions with the following agencies and organizations regarding the NBS program in Biotechnology: President's Office of Science and Technology Policy (OSTP), National Aeronautic and Space Administration (NASA), National Academy of Science (NAS), National Foundation (NSF), House and Senate Committees.

Ditmars, D.

Cooperation with R.A. Robie of the U.S. Geological Survey, Reston, Va., in preparing a sample of pure calcium and measuring the heat capacity of the solid phases from 4 K to the melting point, 1112 K.

Commission on Standardization of Thermophysical Property Measurements of the European Thermophysical Properties Union; this Commission is sponsoring and coordinating the assembly of a two-volume compendium of apparatuses and techniques for the measurement of thermophysical properties. One chapter has appeared in press on a survey of high temperature drop calorimetry; another chapter on hardware design is in preparation.

Physics Department, Brock University, Ontario, Canada; investigation of high-temperature heat capacity of pure aluminum, pure copper.

Interaction with the following concerning research priorities of common interest for environmentally resistant materials at high temperatures: Larry Kaufmann, MANLABS, Cambridge, Massachusetts.

Domalski, E.S.

Cooperative planning with engineers involved in solid waste disposal, solid waste processing, and resource recovery from the ASTM Committee E-38 on Resource Recovery and the ASME Research Committee on Industrial and Municipal Wastes concerning combustion characteristics of waste materials.

Participation in the U.S./U.K. collaboration for Waste Combustion. Tentative plans were made for collaborative research to be conducted on comparison of (1) chlorine content analysis of municipal solid waste, (2) calorific value data derived from U.S. and U.K. kilogram-capacity calorimeters, and (3) combustion studies on threshold conditions for the formation/destruction of chlorinated species.

Development of a research agreement with the U.S. Department of the Army, Chemical Research and Development (CRDC), Aberdeen Proving Ground, Maryland to carry out combustion calorimetry and develop estimation methods for organic phosphorous compounds (CRDC) was begun.

Garvin, D.

CODATA; Preparation of Thermodynamic Data Bases and Tables, jointly with groups at Harwell and University of Sussex (U.K.), University of Grenoble (Fr) and Institute for High Temperatures (U.S.S.R.).

USA/USSR Science Exchange: Exchange of data, calculational methods and interpretations of data between the Chemical Thermodynamics Data Center and a similar group at the Institute for High Temperatures, Moscow.

CODATA analysis of data on aqueous solutions for the Task Group on Key Values for Thermodynamics, and detailed review of their tables of recommended values.

Report on progress of research program for the DoE Pittsburgh Energy Technology Center on critical evaluation of data necessary for flue gas clean-up procedures.

Goldberg, R.N.

Interactions with the following persons have taken place:

Robert H. Wood, University of Delaware, Newark, Delaware, Aqueous Solutions and Thermodynamics.

Joseph Rard, Lawrence Livermore Laboratory, Livermore, California, Aqueous Solutions and Thermodynamics.

Loren Hepler, University of Alberta, Edmonton, Alberta, Canada, Aqueous Solutions and Thermodynamics.

Cecil E. Vanderzee, University of Nebraska, Lincoln, Nebraska, Aqueous Solutions and Thermodynamics.

Peter Tremaine, Alberta Research Council, Edmonton, Alberta, Canada, Aqueous Solutions and Thermodynamics.

Peter Huang, NBS Humidity Standards Division.

Kirchhoff, W.H.

Collaboration with I.W. Levin, et.al., Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes and Digestive and Kidney Diseases, on thermodynamic properties of lipids.

J.D. Fine, Surface Science Division, on the statistical analysis of depth profile sputtering data.

Neumann, D.B.

Collaboration with the following persons have taken place:

J.B. Pedley, University of Sussex, Brighton, England; development of data bases for the thermodynamic properties of inorganic and organic compounds.

Robert H. Wood, University of Delaware, Newark, Delaware; methods for the computer readable transfer of solution data.

B.B. Molino, NBS Office of Standard Reference Data; development of standard storage and retrieval methods for bibliographic information.

K. Marsh, Thermodynamics Research Center, Texas A&M University; chemical thermodynamic data bases for organic species.

Robert Freeman, University of Oklahoma, Publication of the Bulletin of Chemical Thermodynamics.

Parker, V.B.

Collaboration with F. Oetting, Rockwell International and J. Fuger, University of Liege, on the chemical thermodynamics properties of the uranium halides and other actinide halides for IAEA.

Collaboration with members of CODATA Task Group on the preparation of Chemical Thermodynamic Tables.

Collaboration with Malcolm Rand, AERE, Harwell on the chemical thermodynamic properties of actinide halides and thermal functions for calcium and its compounds.

Collaboration with Donald D. Wagman, former NBS staff scientist on CODATA Task Group on Chemical Thermodynamic Key Values and Thermodynamic Tables.

Consultation with E.H.P. Cordfunke, Netherlands Energy Research Foundation, Petten, Netherlands on the chemical thermodynamic properties of the actinide elements and their compounds.

Anthony Mueller, OECD, Paris and Sidney Phillips, Lawrence Berkeley Labs., chemical thermodynamic data base for nuclear waste disposal and re-evaluation of thermodynamic data.

Schwarz, F.

Collaboration with I.W. Levin, National Institute of Arthritis and Metabolic Diseases, NIH on the thermal stability of clathrin. Interaction with I.W. Levin on the thermal properties of the lipids.

Collaboration with A. Shrake, Office of Biologics, FDA on the thermal stability of serum albumin.

Collaboration with C.J. Steer, Laboratory of Biochemistry and Metabolism, NIH on the thermal stability of clathrin.

Interaction with P.D. Ross, National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, NIH, on the calibration and performance of the Hart Differential Scanning Calorimeter.

Interaction with J. Matthews, Genex Corp. on the performance of the Hart DSC and on the use of ribonuclease and lysozyme as potential standard reference materials for calibrating DSC's.

Smith-Magowan, D.

Collaboration with the following persons have taken place:

R.H. Wood, University of Delaware, on the development of methods for the correlation and theoretical interpretation of the thermodynamic properties of aqueous solutions at elevated temperatures and pressures.

S.L. Miller, University of California at San Diego, on the evaluation of Gibbs energies of formation for metabolites of the Krebs cycle.

B.R. Staples, U.S. Bureau of Mines, Albany, Oregon, on the correlation of the thermodynamic properties of calcium chloride and evaluation of Debye-Huckel limiting law parameters for water as functions of pressure and temperature.

D. Ericsson, Energy Concepts, Annapolis, Md., on the thermodynamic properties of aqueous solutions for use as adsorption refrigerants.

Tewari, Y.B.

Henry Zobel, Moffett Technical Center, CPC International, Summit-Argo, IL., procurement and characterization of glucose isomerase for microcalorimetric and equilibrium measurements.

Weber, T.I.

Interactions with the following persons have taken place:

Dr. Sancar Adhya, NIH, on the crystallization and structural studies of E. coli gal repressor.

Professor Herman Ammon, Department of Chemistry, University of Maryland, on structural studies of glutaminase-asparaginases from several bacterial sources.

Dr. Gary Gilliland, Genex Corporation, Gaithersburg, Md., on data collection from crystals of catabolite gene activator protein.

Dr. Alan Peterkofsky, NIH, on the crystal structures of several mutants of catabolite gene activator protein.

Professor Thomas Steitz, Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, CT., on crystallization of rec A protein and on refinement of the structure of catabolite gene activator protein.

Professor Susan Taylor, Department of Chemistry, University of California, San Diego, CA, on the prediction of the structure of the regulatory subunit of mammalian cAMP-dependent protein kinase.

Wlodawer, A.

Collaboration with the following persons have taken place:

Professor Robert Huber, Max Planck Institute, Martinsried, West Germany, on the neutron diffraction studies of the structure of bovine pancreatic trypsin inhibitor and of photosynthetic reaction center.

Dr. Lennart Sjolin, Chalmers Polytechnic, Gothenburg, Sweden, on the structural investigations of ribonuclease and bovine pancreatic trypsin inhibitor.

Dr. Franz Schmid, University of Regensburg, West Germany, on crystallographic studies of porcine ribonuclease.

Dr. David Moss, University of London, England, on comparisons of independently refined structures of bovine ribonuclease.

Professor Herman Ammon, University of Maryland, on crystallographic studies of glutaminase-asparaginases from several bacterial sources.

Dr. Giuseppe Zaccai, Institute Laue-Langevin, Grenoble, France, and Dr. Martin Gellert, NIH, Bethesda, Md., on the low-angle neutron scattering studies of gyrase and gyrase-DNA complexes.

Dr. Ettore Appella, NIH, Bethesda, Md., on crystallization of DNA fragments.

Dr. Joyce Jentoft, Case Western University, OH., on crystallographic studies of the RNA-binding protein from the phage pp12.

Dr. Gary Gilliland, Genex Corporation, Gaithersburg, Md., on crystallographic studies of a sweet protein, monellin.

10. VISITING SCIENTISTS

The Thermodynamics Division has been host to the following scientists who have worked with NBS scientists on problems of mutual interest.

Chandrasekharaiah, M.S., Bhabha Atomic Research Center, Bombay, India discussed thermodynamic properties of uranium, iridium and platinum at high temperatures and high temperature effusion measurements.

Chase, M.W., Dow Chemical Company, Midland, MI, worked on the development of JANAF thermochemical tables and the evaluation and tabulation of thermal functions for calcium and calcium compounds for CODATA Task Group on Chemical Thermodynamic Tables.

DeVoe, H., University of Maryland, College Park, MD, performed measurements of solubilities of non-electrolytes as a function of concentration and temperatures in aqueous solution using high performance liquid chromatography and designed an apparatus for the determination of thermodynamic properties by HPLC methods.

Evans, W.H. - Former NBS employee, is an expert on the evaluation of chemical thermodynamic data of relevance to resource recovery, the design of computer codes for chemical thermodynamics, the preparation of catalogs of evaluated chemical thermodynamic measurements. He is a consultant to the CODATA key values task group.

Harrison, R.W., Yale University, New Haven, CT, Dr. Harrison is working on theoretical methods for the determination of biomolecular structure.

Liebman, J.F., University of Maryland-Baltimore County, Baltimore, MD, completed an evaluation of enthalpies of formation of amino acids, peptides, heterocyclic and related compounds. He is an expert on techniques in estimating thermodynamic properties of organic compounds and on strain energies in organic compounds.

Miller, M., University of Warsaw, Warsaw, Poland, Dr. Miller is working on crystallographic structure of proteins and DNA fragments.

Nuttall, R., Former NBS employee, is an expert on solution thermodynamics and evaluation of thermochemical data. Dr. Nuttall participated in developing the data for electrolyte data bases and catalogs of measurements of thermochemical data.

Pedley, A., Imperial College, London, England, spent time at NBS on the development of interactive software for accessing thermodynamic data bases of organic species and for predicting enthalpies of formation.

Pedley, J.B., School of Molecular Sciences, University of Sussex, Brighton, England, spent time at NBS on the development and interactive communication with a data-base on enthalpies of formation of organic compounds, the development of estimation methods for calculating enthalpies of formation of organic compounds and the thermodynamic properties of transition metal chlorides.

Savage, H., National Institute of Health, Bethesda, Md., Dr. Savage is working on neutron diffraction of protein hormones and the structure of bound water in biological systems.

Schumm, R.H., Former NBS employee, is an expert on the evaluation of thermochemical data. Mr. Schumm evaluated data on sulfur compounds relevant to flue gas desulfurization.

Thompson, P.T., Swathmore College, Swathmore, PA, Dr. Thompson is an expert on the interaction of organic species with water in terms of hydrophobicity. He is performing both experimental and theoretical research during his sabbatical at NBS.

Wagman, D.D., Former NBS employee, is an expert on the evaluation of thermodynamic data. Mr. Wagman has prepared the CODATA key values for thermodynamics.

Wasik, S.P., Former NBS employee, is an expert on the evaluations of solubility data for organic species in aqueous and mixed media. Dr. Wasik evaluated data on the thermodynamic properties of alkanes in aqueous media.

Weber, I., University of Maryland, College Park, MD, Dr. Weber is working on the molecular structure of complex biomolecules using both x-ray and neutron diffraction.

Wood, R.H., Chemistry Department, University of Delaware, Newark, DE, worked with the staff on solution thermodynamics, theory and experiment; electrolyte theory of weak electrolytes, speciation calculations, molecular interactions in solution; and the solubilities of non-electrolytes in aqueous solution as a function of concentration and temperature.

MOLECULAR SPECTROSCOPY DIVISION

A. Weber, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

1. INTRODUCTION

A. Goal

This Division is a discipline oriented unit and its goal is to be at the forefront of modern theoretical and experimental spectroscopy in order to:

- Advance spectroscopic measurement methods and techniques
- Develop models, theoretical concepts and quantum theoretical methods for predicting molecular properties and interactions
- Obtain reliable reference spectroscopic data for NBS, government, research community and industrial needs
- Understand and model fundamental chemical processes
- Provide state-of-the-art frequency standards
- Transfer forefront spectroscopic expertise to other NBS Divisions, other government agencies, industry and the research community.

Within the framework of these general goals the Division also follows three specific thrusts which are part of the overall program of the Center for Chemical Physics - Properties of Weakly Bonded Systems, Biotechnology, and Energy Transfer. Properties of weakly bonded systems are obtained for small atomic and molecular complexes held together by van der Waals and hydrogen bond forces in order to develop a data base to understand conformation, thermodynamics, and reactivity of such systems. The objectives of our thrust in biotechnology are to develop and implement methods for the study of metal interactions in proteins and nucleic acids using primarily quantum mechanical techniques, while the major effort of the energy transfer thrust has been directed to the study of vibrational energy transfer.

This summary contains a report of the activities of each of the three groups within the Division during the past year and demonstrates how they are meeting the above objectives.

B. Organization

To carry out its work the Molecular Spectroscopy Division is organized into three working groups: High Resolution Spectroscopy (HRS), Laser Photochemistry (LPC), and Quantum Chemistry (QC). The permanent Division staff is augmented by that of postdoctoral fellows and guest workers. During the past year we have had thirteen guest workers and seven postdoctoral fellows engaged in Division projects. In addition, two members of the Surface Science Division participated in the work of the LPC group. A list of the guest workers, their permanent affiliations, and their activities is given in Section 10 of this report.

C. Division Programs

With the technological advances of micro- and main frame computers and the development of tunable dye and diode lasers that have taken place during the last eight years, the fields of experimental molecular spectroscopy and theoretical quantum chemistry have grown rapidly.

To be able to respond to the present and projected needs of NBS, the Center for Chemical Physics (CCP), and the user community, a significant fraction of the Division's effort must be directed toward achieving and maintaining the expertise of its staff in their discipline oriented fields, and into maintaining its experimental facilities at the state-of-the-art level. We must remain at this level of expertise in spectroscopic measurements, theory, and interpretation in order to respond quickly to provide standards, serve national technical needs, and to insure adequate response to future, unknown problems. The soundness of this approach is justified by the past and present applications of experimental and theoretical spectroscopy by our Division. These applications also provide much of the direction and motivation for our efforts. Remote sensing for industrial and atmospheric monitoring, laser isotope separation and fusion, laser chemistry, and combustion diagnostics are a few of the many important high-technology areas that depend on modern spectroscopic techniques.

In order to meet the calibration and standards requirements for the design and application of tunable infrared lasers and Fourier transform instrumentation over the next decade, several frequency standards activities are pursued in collaboration with several groups from within and outside NBS. A project on spectral frequency standards is undertaken jointly by scientists from the Time and Frequency Division of NBS/Boulder and members of the HRS group. Details about our Calibration Standards work are given in Section 2.B.

There has always been a need for accurate intensity parameters for molecular transitions. Recently these needs have been emphasized and the requirements for accuracy enhanced in connection with the determination and monitoring of trace atmospheric species. Accordingly we are now engaged in the determination of accurate transition moments, line

strengths, and line broadening parameters of several molecular species which are believed to play an important role in the chemistry of the earth's atmosphere (see Section 2.C)

We continue to be involved in the spectroscopy of the environmental and space sciences. Our work is directed toward the broadening of the data base upon which spectroscopic measurements of trace atmospheric constituents by means of ground based, balloon and satellite borne instruments are performed and evaluated. This, as well as similar efforts of interest to various branches of NASA and other user groups, is part of our continuing involvement in problems of national concern. Details about these and other activities may be found in Section 2.C.

Our Division has significant other agency contracts with Air Force Office of Scientific Research (AFOSR), Department of Energy (DOE), National Aeronautics and Space Administration (NASA), Chemical Manufacturers Association (CMA), and the National Foundation for Cancer Research that help these agencies fulfill their missions. Details are discussed in the group reports. These efforts along with the lists of consultations, talks, publications, and collaborative activities show our strong coupling with industry, other government agencies, and the research community.

The above constitutes only a sample of our involvement and response to the needs of the user community. Our Division is host to several guest workers from universities, other government agencies, and from overseas countries (see Section 10). The numerous and varied interactions and collaborations of the Division's staff with non-NBS scientists and user groups are detailed in Section 9 - Professional Interactions, Consulting and Advisory Services.

During the past year efforts of the LPC group have been redirected and have acquired a stronger focus in the quantum-state specific studies of molecular dynamics, especially in the role played by energy transfer in the spectroscopy and kinetics of molecules in the condensed phase. Investigations of energy transfer from vibrationally excited bonds in liquids and solids, as well as in molecules bound to solid surfaces are described in Section 3.B. As an outgrowth of the work done in previous years on infrared multiphoton dissociation experiments, new work has been started on the dynamics of van der Waals complexes, especially on vibrational predissociation (see Section 3.D). These experiments, performed in the time domain, measure directly the vibrational lifetimes and supplement the work done in the frequency domain in which lifetimes are inferred from spectral line widths (see Section 2.D as well as earlier descriptions in the FY'83 and '84 Annual Reports).

Work was also carried forward in Matrix isolation spectroscopy (Section 3.E) and the desorption of molecules from surfaces (Section 3.C). Thermal desorption of molecules chemisorbed on well characterized surfaces were studied with a dedicated facility incorporating several techniques for surface sensitive analysis, a computer controlled data acquisition

system and a laser probe system with sub-Doppler resolution capability. Since thermal desorption takes place slow enough to be modelled as an equilibrium process, new work has been started on fast desorption brought about by rapid heating of the surface by non-resonant laser radiation.

The field of Quantum Chemistry has in recent years experienced significant new developments which extend the range of reliable and useful calculations to complex polyatomic systems. A new program to attack the problems of the stabilities, conformations, spectroscopy and reactivity of complex molecules, clusters, ions, radicals, and transition states, among others, was successfully conducted for the third year by the Quantum Chemistry group. The ability of the QC group to attack large scale computational problems using ab-initio rather than semi-empirical methods has been significantly enhanced through the acquisition of an IBM-4381 superminicomputer which forms the core of the newly formed Molecular Structure and Modeling Facility of the Molecular Spectroscopy Division. Details of the activities of the QC Group are given in the group report.

In the Annual Report for 1982 we described the results of our initial work on the spectroscopy of molecular complexes in the gas phase. This initial work, on the rotation-vibration spectrum of the hydrogen-bonded HF-dimer has been expanded since that time to include the study of a variety of hydrogen-bonded and van der Waals complexes by all three groups of the Division. Thus, detailed investigations are underway with new instrumentation of microwave and infrared high resolution spectra (see the reports by the High Resolution Group in Section 2.D). The measurements for these investigations are made in the frequency domain and knowledge about the lifetimes of excited states is had only by inference from the widths of the spectral lines. Direct information about lifetimes and, especially, pre-dissociation rates is obtained from measurements made in the time domain; these are performed in the Laser Photochemistry Group and are reported in Section 3.D. These experimental efforts are often done in conjunction with work done in the Quantum Chemistry Group (see report 4.B.2). The study of weak chemical interaction as exemplified by the hydrogen bonding and van der Waals forces is of considerable interest for the present and the foreseeable future (see the Pimentel Report "Opportunities in Chemistry", National Academy Press, Washington D. C., 1985) and our Division is expected to fully participate in this field during the coming years.

The research described in the following report was performed in a cooperative manner between the permanent staff of the Division, NBS/NRC postdoctoral research associates, and guest-scientists from the U.S. and abroad. Close collaboration also exists with members of the Surface Science Division of the Center for Chemical Physics in areas of picosecond spectroscopy, spectroscopic studies of surface desorption processes, and energy transfer.

2. HIGH RESOLUTION SPECTROSCOPY GROUP

J. W. Bevan, J. T. Hougen, B. J. Howard, D. E. Jennings,
W. J. Lafferty, R. W. Lovejoy, F. J. Lovas, A. G. Maki, I. M. Mills,
N. Ohashi, W. B. Olson, A. S. Pine, G. Rotter,
R. D. Suenram, G. A. Thompson, A. Weber, B. A. Wofford

A. Introduction

The work of this group involves experimental and theoretical applications of molecular spectroscopy for characterizing gas phase molecules, primarily in the infrared (rotation-vibrational) and microwave (rotation-al) spectral regions, the development of frequency standards for the infrared, and the development and application of new experimental techniques for high resolution spectroscopy. The emphasis of these studies is in the applications of our expertise to problems in structural chemistry, atmospheric chemistry, chemical analysis, radio astronomy and the properties of novel molecular species, particularly floppy molecules.

The major activity of the Molecular Spectra Data Center, supported by the Office of Scientific Reference Data (OSRD) is to provide evaluated data on molecular rotational spectra in the microwave region and to develop evaluated infrared spectra to be used as standards in calibrating diode lasers and infrared laser spectrometers. This work is based on the needs of the user community. Thus the work on infrared standards is a response to requests from the instrumentation industry, industrial research laboratories, applied technological user groups, and government agencies and laboratories. Improvements in the stability of diode lasers have emphasized the need for accurate calibration standards. The absorption frequencies of N_2O that involve the lower energy levels are now being tied to the cesium frequency standard. This work has been made possible through the joining of the unique facilities of the Time and Frequency Division of NBS/Boulder with our spectroscopic expertise. Other collaborations, with non-U.S. research groups exist as well in an effort to develop the most extensive and accurate set of frequency calibration data.

Molecular radioastronomy continues to demand accurate laboratory microwave data and spectroscopic expertise and the measurement, critical evaluation, and dissemination of microwave data of astrophysical interest is being continued. Our collaboration with radio-astronomers provides the contacts and experience necessary to insure that these evaluations and compilations are both practical and useful.

The environmental problem posed by the pollutants of the earth's atmosphere, especially the role played by trace constituents in the chemistry of the upper atmosphere, are of major concern and a portion of the group's activities is devoted to providing critically needed data to help solve some of these problems. In this effort our activities are guided by the needs of the environmental research community, and are

conducted with the support of NASA and the Chemical Manufacturers Association. These efforts will continue to play an important role in our work during the coming years.

Weakly bound molecular complexes, i.e. van der Waals and hydrogen bonded molecules have received considerable attention in our laboratory during the past year and will continue to do so in the future. The group is in a unique position of having available personnel and instrumentation that permits such studies to be performed using any and all of the facilities from the microwave to the near infrared region of the spectrum in a concerted attack on the problems posed by these weakly bound systems.

The work conducted during the past year has been aided through the efforts of a number of guest-scientists from the U.S. and abroad. Moreover, sustained collaboration with non-NBS groups serves to disseminate the results of our work in the quickest and most far reaching way to the user community. Such collaboration also benefits our work through access to data and facilities not presently available at NBS. Particularly noteworthy among the non-NBS institutions with which beneficial collaborations have occurred during the past year are: The University of Oulu, Oulu, Finland, The University of Illinois, The University of Alberta, Texas A&M University, Lehigh University, Oxford University, Oxford, England, The University of Reading, Reading, England, The National Research Council of Canada, The Institute of Molecular Science, Okazaki, Japan, Kanazawa University, Kanazawa, Japan, The Harry Diamond Laboratories of the U.S. Army, The NASA-Greenbelt, NASA-Langley NASA-Goddard, and NASA-Ames Laboratories, and The National Solar Observatory at Kitt Peak, AZ.

In the following the group's activities are described according to the three broad topics of calibration and Data Center activities, environmental problems, and spectroscopy of weakly bound molecular complexes. In addition to these programmatic activities there were others of a more general and varied nature, including several studies in the field of mathematical physics by one of our guest workers. These are described in the fourth section under General Spectroscopy and Theory.

B. Calibration and Data Center Activities

We collect under this heading the work of the group connected most closely with the core mission of NBS, namely the production and dissemination of compilations of accurately measured frequencies or wavenumbers for use as secondary standards, of compilations of critically evaluated molecular constants for use in other disciplines, or occasionally of spectral fitting programs, for use in reducing data in other laboratories. The group devotes a significant portion of its effort each year to this program, and frequently collaborates with workers in other laboratories. Outputs of the program serve needs in both the infrared and microwave spectral regions.

1. Tying the Lower Vibrational Levels of N_2O to the Cesium Frequency Standard

(A. G. Maki and J. W. Wells)

Our continuing collaborative effort with Dr. J. W. Wells (NBS Boulder) this past year has seen some new frequency measurements that were the key to tying all the lower vibrational energy levels of N_2O to the cesium frequency standard. These levels previously had been measured using wavelength measurement techniques, but now we have independent frequency measurements of these levels. One of the most satisfying aspects of this work was the incorporation of the very accurately measured N_2O laser frequencies.

The new measurements that were made in Boulder involved the $00^{\circ}1-00^{\circ}0$ and $01^{\circ}1-01^{\circ}0$ transitions of N_2O which were measured against a CO laser local oscillator in the 1257 to 1340 cm^{-1} region. The CO frequencies were in turn measured with respect to combinations of CO_2 laser frequencies. Since the well measured N_2O laser frequencies involved the $10^{\circ}0-00^{\circ}1$ transition, combining these measurements gave accurate frequency values for the $10^{\circ}0-00^{\circ}0$ transitions between 2135 and 2268 cm^{-1} (see Fig 2.1).

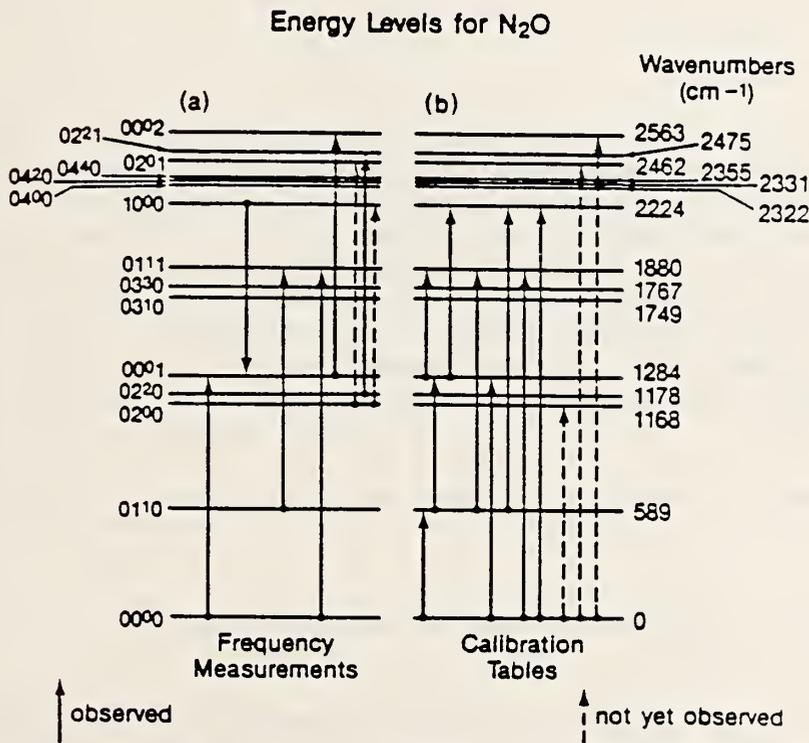


Figure 2.1. Energy level diagram that illustrates on the left (a) the frequency measurements that have been made on the lower levels of N_2O (solid arrows), or that we hope to make (dashed arrows). On the right (b) are the resulting calibration tables that can be prepared based on the frequency measurements.

Also, combining the new 01¹1-0110 measurements with earlier ones on the 01¹1-00⁰ transitions gave us good frequency values for the 01¹0-00⁰ transitions near 590 cm⁻¹. These new frequency measurements have been combined with older frequency measurements and with other microwave and infrared data that determined some of the rotational constants for the various states to obtain the best term values for the lower vibrational states of N₂O, all related to the cesium frequency standard. These term values are being used to prepare the infrared calibration atlas for N₂O described in the next section.

In the coming year we expect to be able to measure some of the weaker hot band lines in the 1285 cm⁻¹ band of N₂O to obtain term values that will provide frequency calibration in the 2000-3000 cm⁻¹ region. Our long range goals also include the measurement of hot bands accompanying the laser transitions near 940 cm⁻¹ and the frequency measurement of some lines due to the 10⁰0-02⁰0 transitions near 1060 cm⁻¹. Finally, with a little bit of luck it may be possible to obtain a diode with enough power in a single mode to make a few saturated absorption measurements on the 1285 cm⁻¹ band of N₂O. That would give an order of magnitude improvement in the accuracy of the frequency measurements.

2. Infrared Calibration Atlas (A. G. Maki)

During the past four or five years we have been developing infrared spectral frequency tables for calibrating tunable IR laser spectrometers. We have worked with several groups in obtaining highly accurate heterodyne and Fourier transform spectra on many bands of the OCS and N₂O molecules which will form the basis of two reviews. Much of the manuscript and tables for the OCS review were completed previously. The new results on the ν_2 band will be added to the existing tables to complete this review. During the past year further heterodyne measurements on N₂O bands up to 2200 cm⁻¹ have been obtained (see preceding section) and allow calibration tables to be produced in the regions of 520 cm⁻¹, 930 cm⁻¹, 1300 cm⁻¹, 1880 cm⁻¹, and 2200 cm⁻¹ with each covering a range of 90-150 cm⁻¹. Some additional measurements needed for calibration near 2700 cm⁻¹ are being sought to complete the analysis and produce a set of tables which will replace the previous publication on N₂O in the Journal of Chemical and Physical Reference Data. This work is supported by the OSRD.

3. Revised Recommended Rest Frequency List (F. J. Lovas)

In May 1985 the manuscript entitled "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions - 1984 Revision" was submitted to J. Phys. Chem. Ref. Data by F. J. Lovas. This is a complete revision and update of a 1979 publication in Astrophys. J. Supplement by F. J. Lovas, L. E. Snyder, and D. R. Johnson. The reported astronomical observations of new species and new rotational transitions of previously identified molecules has more than tripled the number of lines reported in the first publication.

Preprint copies of this manuscript have been distributed to the nearly 300 astronomers and spectroscopists on our mailing list with the request that they examine it for oversights or errors. A number of useful responses have already been received. In fact among the responses was a preprint of a survey of Orion A between 247 GHz and 263 GHz which contains more than 200 new transitions which were added to the table. We have also filled a request for a magnetic tape copy of the data file to be used on the new British - Dutch 15-metre submillimeter wave telescope being constructed on Mauna Kea, Hawaii. The most pleasing aspect of the responses has been the interest of the astronomy community in the accuracy of the reported information as well as providing new observations to keep it as up-to-date as possible. The manuscript has been submitted to J. Phys. Chem. Ref. Data and the major tables of data have been converted via a magnetic tape to the Bedford system used by OSRD. This work is supported by the OSRD.

4. Microwave Spectral Tables (R. D. Suenram and F. J. Lovas)

We continue to carry out the general literature search for all published (and unpublished) microwave spectra for this project. Evaluation and coding new data continues on the diatomic and triatomic species to keep the computer files from the earlier publications current.

Work on the third publication of the Microwave Spectral Table series "Hydrocarbons" is progressing. The spectral fittings of all the normal symmetric top and asymmetric top species are complete. The corresponding data files of the measured and predicted spectra have been produced and all isotopic and vibrational species have been coded. The analysis of the species with internal rotation remains to be accomplished since the programs for these analyses were not fully implemented on the Univac. Since we have moved all programs and data files to NBS's new Cyber computer, implementation of these programs on the Cyber is in progress. This work is supported by the OSRD.

5. Supplement to Structural Data Tables for Polyatomic Molecules (W. J. Lafferty)

Ten years ago members of the Molecular Spectroscopy Division collaborated with spectroscopists from Japan, Germany and England to produce a set of structural tables of polyatomic molecules. All structures obtained for gas phase molecules by electron diffraction and infrared, Raman, electronic, and microwave spectroscopy were included. The tables were published by Landolt-Börnstein in their New Series (Group II, Volume 8).

This year we have updated these tables. The literature has been searched from 1974 to the beginning of 1985. All new structures as well as structures whose parameters have been significantly improved have been included in the tables. The entry for each molecule includes the

structural parameter as well as a schematic drawing of its structure. This supplement will once again be published by Landolt-Börnstein. This work is supported by the OSRD.

6. Review of SO₂
(F. J. Lovas)

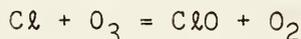
After several years in the process, the publication of a review on the spectrum of SO₂ is forthcoming in J. Phys. Chem. Ref. Data Vol. 14 (1985). This is part 22 of the series "Microwave Spectra of Molecules of Astrophysical Interest." This work is supported by the OSRD.

C. Spectroscopy for Environmental Studies

Many small molecules play a significant role in the chemistry of the earth's atmosphere. As such, they are of significant interest to agencies like NASA, DOD and the CMA (Chemical Manufacturers' Association). The interest of the latter agencies generally focusses on molecular spectroscopy as a remote sensing tool and for the determination of concentration profiles. Consequently, the emphasis in this section is not on band analyses per se, but rather on line intensities, line widths, line shapes, and the effect of pressure on these quantities. As in all branches of spectroscopy, the very narrow band width of infrared laser sources now permits quite reliable studies of phenomena involved in spectroscopic concentration determinations.

1. High Resolution Spectrum of the ν_2 and ν_3 Bands of HOCl
(W. J. Lafferty and W. B. Olson)

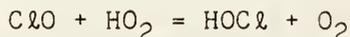
Our interest in the spectrum of HOCl has been motivated by very practical reasons. Cl atoms produced from the photolysis of freons in the upper atmosphere react with stratospheric O₃ via the routes:



and



There are a great number of competing reactions in the stratosphere, and the extent of the damage done by the freons is at this point still controversial. HOCl can be produced from ClO by the reaction



which, if the HOCl formed is sufficiently stable, serves to withdraw Cl atoms from the chain reaction.

The stability of HOCl in the upper atmosphere is still somewhat uncertain. A number of laboratory studies have been carried out on these and other reactions, but it appears that the most practical way in which

to get a handle on the role played by HOCl in stopping or slowing the ozone destroying chain reactions is to directly observe this species in the stratosphere and directly monitor its concentration.

A number of unsuccessful attempts to detect HOCl with both ground based and balloon spectrometers have been made. One of the problems of detection of this molecule arises from that fact that even in the atmospheric windows, the HOCl absorption bands are overlapped by the lines of very minor stratospheric constituents which have about the same intensities expected from the lines of HOCl.

In order to positively identify the lines arising from the HOCl spectrum, it is necessary to have very precisely known line frequencies since only a few lines of a band may fall in a clear spot in the spectrum. We, therefore, with the partial support of the Chemical Manufacturers Association, have recorded and assigned the two lowest frequency bands of HOCl with the NBS BOMEM FTS spectrometer with a resolution of 0.004 cm^{-1} . Careful attention has been given to frequency calibration; fortunately, both bands fall in regions where there are very well measured calibration lines. The ν_2 band centered at about 1220 cm^{-1} , was calibrated against N_2O while the ν_3 band was calibrated against CO_2 absorption lines. The absolute frequency calibration of the BOMEM spectrometer was found to be surprisingly good. Corrections of only a few ten thousands of a cm^{-1} were found to be necessary. We conservatively estimate that the absolute precision is better than $\pm 0.0005 \text{ cm}^{-1}$; the relative precision is somewhat better, and is on the order of 0.00002 cm^{-1} .

Both ν_2 , the bending vibration, and ν_3 , the Cl-O stretching mode, are a-type bands. Figure 2.2 shows a much compressed scan over the ν_2 band.

The assignment is complicated by the presence of two chlorine isotopes, but line assignment presented no difficulties; a very complete assignment has been accomplished for both bands of both isotopic species. The observed lines have been fit using a Watson Hamiltonian, and the standard deviation of the fittings for all the bands was 0.0002 cm^{-1} .

Currently relative line intensities are being measured for both bands in order to determine the magnitude of the Herman-Wallis effect on the intensities. When this is completed, line intensities will be computed, and a band atlas including line frequencies and line strengths at several temperatures will be produced. This work is supported by CMA.

2. Measurements on the ν_3 and ν_4 Bands of Nitric Acid (HNO_3) (A. G. Maki)

The ν_3 and ν_4 bands of nitric acid were investigated in collaboration with Prof. A. Fayt of the University of Louvain - la Neuve, Belgium. We have used the NBS BOMEM interferometric spectrometer to measure the

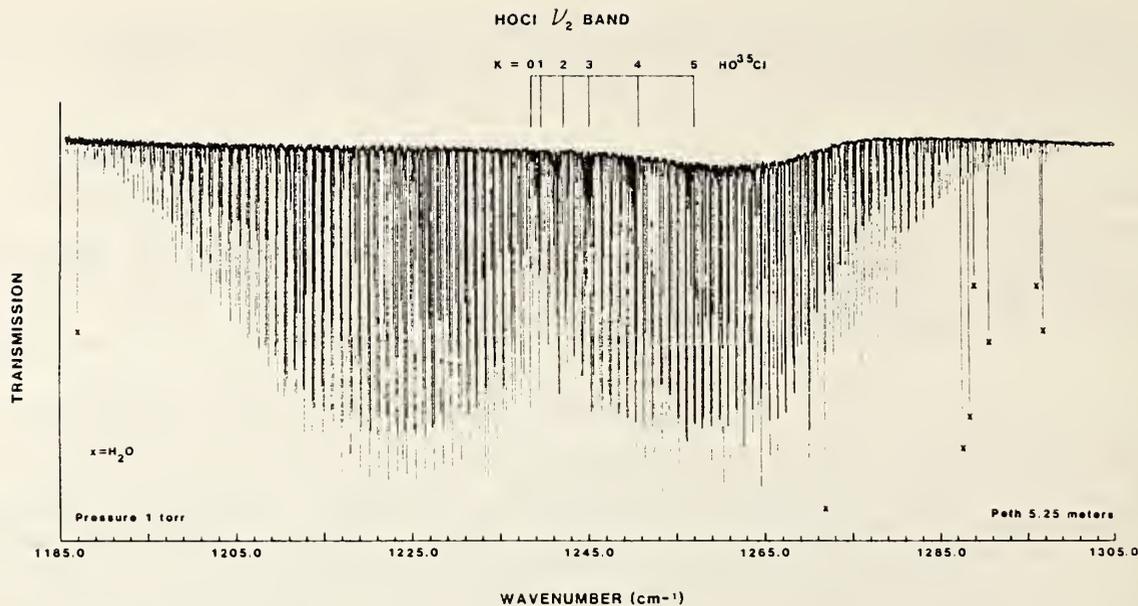


Figure 2.2 The ν_2 band of HOCl recorded under full instrumental resolution of 0.004 cm^{-1} . The sub-band centers of the major isotopic species are labelled at the top.

spectrum of nitric acid (HNO_3) in the 1250 to 1360 cm^{-1} region which includes the ν_4 band at 1303 cm^{-1} and the ν_3 band at 1326 cm^{-1} . In collaboration with Dr. Andre Fayt transitions for both of these bands have been assigned and fit to appropriate asymmetric rotor constants.

These bands are used by certain laboratories for atmospheric measurements since they fall in a spectral region where the atmosphere is relatively transparent. It is important that the rotational line structure of these bands be understood so that modeling calculations can be used to simulate atmospheric spectra both to interpret the atmospheric distribution of nitric acid, and also to cancel out the nitric acid features when searching for underlying transitions due to other atmospheric species, such as chlorine nitrate.

To supplement the BOMEM spectrum we have also measured diode laser spectra for several small spectral regions in order to resolve some of the more tightly clustered features such as the ν_4 Q-branch. Figure 2.3 shows an example of the diode laser spectrum of ν_4 . Although only the $K_0=0,1$ transitions are labelled many other features seen in the figure have been identified and assigned.

Thus far the spectra have been fit with a standard deviation of about 0.002 cm^{-1} . It is not clear if the fit could be improved by including some interactions with nearby bands. In the coming year we hope to obtain some laser diode spectra of the ν_3 band of HNO_3 in order to see if some of the

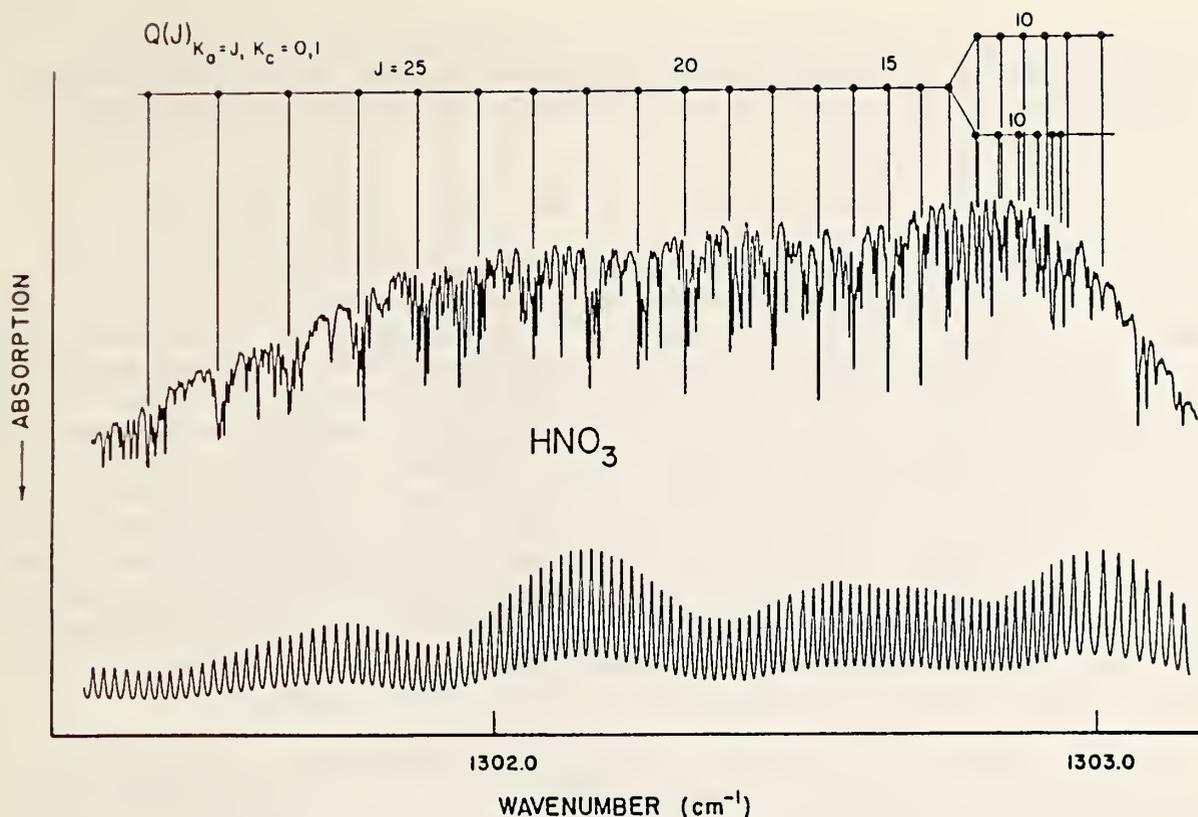


Figure 2.3. Diode laser spectrum of the ν_4 Q-branch for nitric acid (HNO_3). The lower trace is the fringe pattern from a solid germanium étalon; FSR = 0.016cm^{-1} .

more obvious deviations are artifacts due to incompletely resolved clusters of lines. It appears, however, that there should be a weak $\Delta k=2$ interaction between ν_3 and ν_4 similar to what we have found between ν_5 and $2\nu_9$. This work is supported by NASA.

3. New Intensity and Frequency Measurements on ClO (A. G. Maki, and G. A. Thompson)

Chlorine monoxide (ClO) is one of the reactive intermediates involved in the chlorine cycle in the atmospheric chemistry that governs the concentration of ozone in the upper atmosphere. Much interest centers on measurements of the concentration of ClO in the atmosphere and a number of techniques have been used to try to measure the concentration of ClO in the atmosphere.

At the present time microwave techniques seem to have been most successful in determining the concentration of ClO in the upper atmosphere but there is an apparent disagreement between the ground based microwave measurements^{1,2} and the ground-based infrared measurements.³ In particular, the ground-based measurements of Mumma *et al.*³ failed to detect any ClO although the expected column density was expected to give a detectable signal. Since it has been suggested that errors in either the

frequencies or the intensities of the ClO lines might contribute to the non-observation of ClO in the Mumma *et al.* experiments, we have undertaken an independent remeasurement of the intensities and frequencies of the ClO spectrum in the infrared.

Accurate intensity measurements are not easy to make on stable molecules and are even more difficult for unstable molecules since it is normally necessary to know how many molecules are present in the absorption path. The microwave measurements do not have this problem since the microwave absorption intensity is proportional to the square of the dipole moment and the dipole moment can be measured quite accurately from the Stark effect. The several measurements that have been made of the infrared intensity indicate that it is relatively weak and for that reason Dr. Chackerian (NASA/Ames) has suggested the possibility that the Herman-Wallis effect, which relates the infrared band intensity to the ratio of the intensity of R-branch transitions to the intensity of the P-branch transitions, can be used to determine the transition moment (infrared intensity) without measuring the ClO concentration. Since the measurement of the ClO concentration is quite difficult, we believe that such a technique that by-passes that one difficult and controversial step merits further investigation and we have begun such a study.

What we plan to do is measure the intensity ratio of P- and R-branch transitions that arise from the same energy levels (in order to eliminate any temperature dependence). For maximum accuracy these measurements must be made under identical operating conditions for both the R-line and the P-line. We plan to switch back and forth between measurements of the R-line intensity and the P-line intensity several times in order to verify that the operating conditions are indeed identical. This work is supported by NASA.

Table 2.1 gives an example of the intensity ratio expected for the different band intensities suggested by various other papers.

Table 2.1. R- and P- Branch Intensity Ratio Calculated for ClO for Different band Intensities.

Band Intensity ($\text{cm}^{-2} \text{atm}^{-1}$)	32.0	11.8	5.0
Intensity Ratio R(16.5)/P(16.5)	1.243	1.334	1.469

Finally, this project also includes a re-measurement and re-analysis of the infrared frequencies of the ClO absorption lines in order to improve the reliability of the calculated infrared spectrum of ClO.

- (1) A. Parish, R. L. DeZafra, P. M. Solomon, J. W. Barrett, and E. R. Carlson, *Science* 211, 1158 (1981).
- (2) P. M. Solomon, R. deZafra, A. Parish, and J. W. Barrett, *Science* 224, 1210 (1984).

(3) M. J. Mumma, J. D. Rogers, T. Kostiak, D. Deming, J. J. Hillman, and D. Zipoy, *Science* 221, 268 (1983).

4. Self-Broadening in the Fundamental Bands of HF and HCl
(A. S. Pine and A. Fried (CAC))

In collaboration with Dr. A. Fried of the Center for Analytic Chemistry, the self-broadened lineshapes have been measured for the fundamental bands of HF and HCl with the high-resolution tunable difference-frequency laser spectrometer in the Molecular Spectroscopy Division. This is a continuation of a project to improve the data base on the spectral band parameters (intensities, self- and N₂- and air-broadened lineshapes and shifts) in support of the NASA Upper Atmospheric Research Program (Project HALOE) to monitor ozone depletion caused by reaction with halogen-containing molecules. Using the narrow-linewidth (~1 MHz) linear-scan-controlled tunable laser system, we observed spectral lineshapes free of instrumental distortion that exhibited deviations from the usual Voigt profile due to collisional (Dicke) narrowing. In Figure 2.4

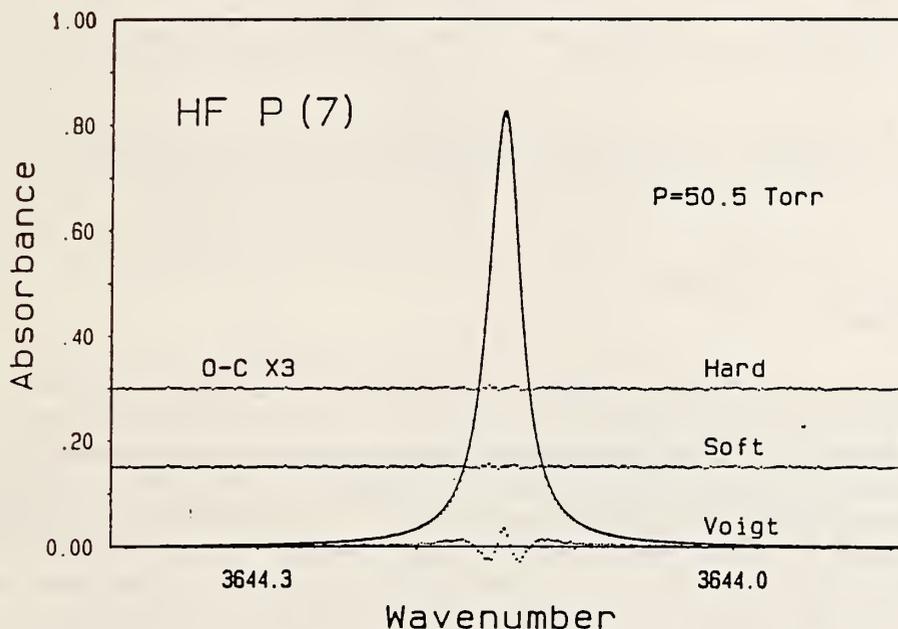


Fig. 2.4. Self-broadened lineshape of the P(7) line of HF compared to various collisional models.

we show an example of the P(7) line of HF at 50.5 Torr least-squares fit by a Voigt function and by the "soft" and "hard" collisional narrowing models which yield much reduced obs.-calc. residuals. The self-broadening coefficients and shifts for the $v=1+0$ transitions of HF and HCl are displayed in Figure 2.5. No significant differences were found for the two chlorine isotopes in the natural abundance sample. Particular care was taken in sample handling for these reactive, readily polymerizable, gases to ensure accuracy, linearity and reproducibility in the pressure and broadening measurements. This work is supported by NASA.

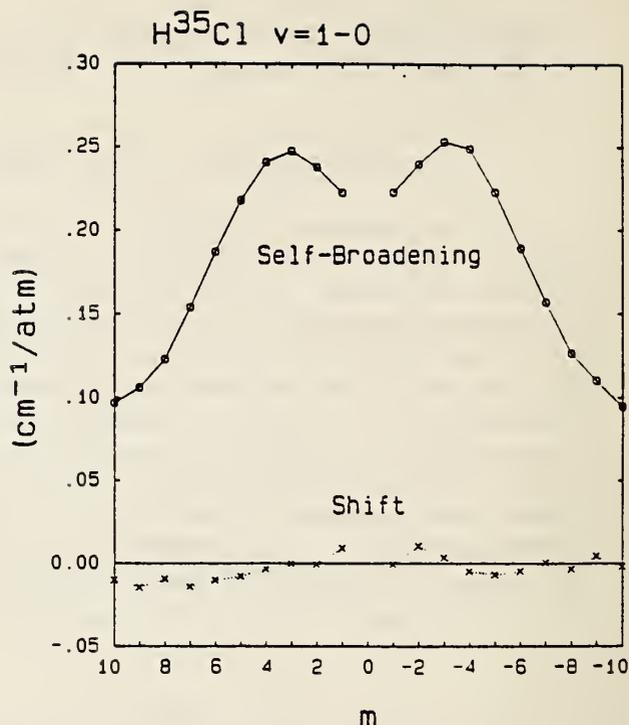
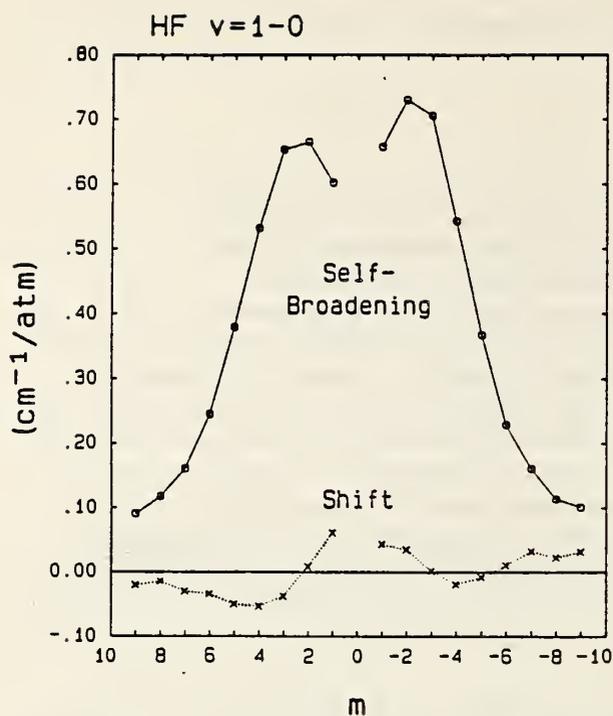


Fig. 2.5. Self-broadening coefficients and shifts for HF and HCl at $T=295\text{K}$.

5. Analysis of the Spectrum of H_2O_2 (W. B. Olson)

The pooling of our data for hydrogen peroxide with those of Prof. Robert Hunt of Florida State University has led to some reassignments of the absorption lines in the OH stretching region of the spectra, and to a direct determination of energy differences between ground state rotational levels and the levels perturbing them, up to $J = 25$ on the most perturbed levels (ground state $K = 8$). The previous limit was $J = 15$. These reassignments were made possible by a clarification of the group theory, and enumeration of the types of perturbations possible in hydrogen peroxide, provided by the permutation-inversion group theory treatment of hydrogen peroxide by J. T. Hougen.¹

In addition to extending assignments, it has been possible, using Hougen's symmetry treatment, to introduce some reforms in terminology and notation for hydrogen peroxide energy levels and transitions which we feel will greatly simplify the understanding of hydrogen peroxide, and greatly facilitate verbal and written communication. The basis of the new terminology is a two valued overall symmetry level (U for ungerade and G for gerade), for the two torsional substates for a given principal torsional quantum number, rather than the old four valued numerical τ label.

Selection rules for transitions had been worked out in terms of the τ labels, but these had no direct connection with overall symmetries, and this led to considerable confusion as to the source of perturbations when these were evident. A preliminary account of this work has been given in a report to NASA.

A coupled asymmetric rotor program for simultaneous fitting of combination differences in the ground state (OG) and perturbing first excited torsional state (1G) was expected to be available in Sept. 1984, but was delayed, and is now expected to be available in Sept. 1985. Fitting of our data with this program should lead finally to a definitive set of ground state rotational constants for H_2O_2 . This work is supported by NASA.

(1) J. T. Hougen, Can. J. Phys. 62 1392-1402 (1984).

D. Spectroscopy of Hydrogen-bonded and van der Waals Complexes

The program of study of hydrogen-bonded and van der Waals complexes initiated several years ago now represents about 25% of the group's total effort. In addition to studies using a difference frequency laser spectrometer in the 3 micron region, this year brings forth studies using the BOMEM Fourier transform spectrometer in both the mid- and far-infrared, studies using the new pulsed Fourier transform microwave spectrometer (Flygare type), as well as theoretical studies. This program has benefitted greatly this past year from collaborations with guest workers. We certainly plan to continue work in this direction for the foreseeable future.

1. Hydrogen Bond Energies of the HF and HCl Dimers (A. S. Pine and B. J. Howard)

The dissociation energies of the hydrogen-bonded complexes, $(\text{HF})_2$ and $(\text{HCl})_2$, have been obtained from high-resolution measurements of absolute infrared line strengths at a single temperature and pressure under the assumption of minimally-perturbed local-mode behavior of the outer hydrogen stretch. The measurements were made with a difference-frequency laser system on low pressure (P-1-2 Torr) gas samples cooled to near the condensation point (T-219 K for HF, T-127 K for HCl) in a long path (L-64-80 m) White cell. The observed absolute intensity pattern of the ${}^r\text{Q}_0$ subbranch of the outer or "free H" stretching band, ν_1 , of $(\text{HF})_2$ is shown in Figure 2.6 along with a simulated trace based on the usual Hönl-London and Boltzmann factors for the J assignments and tunneling splittings obtained in our previous work. The transition lineshapes in the simulated trace are Voigt profiles obtained by convolving the calculated Doppler distribution with a pressure-broadened Lorentzian of half-width = 34 MHz. The agreement between the observed and calculated spectra is excellent as can be seen in the subtracted residuals trace of the bottom of Figure 2.6 which exhibits only the ${}^r\text{R}_0$ lines and some hot band structure not included in the model.

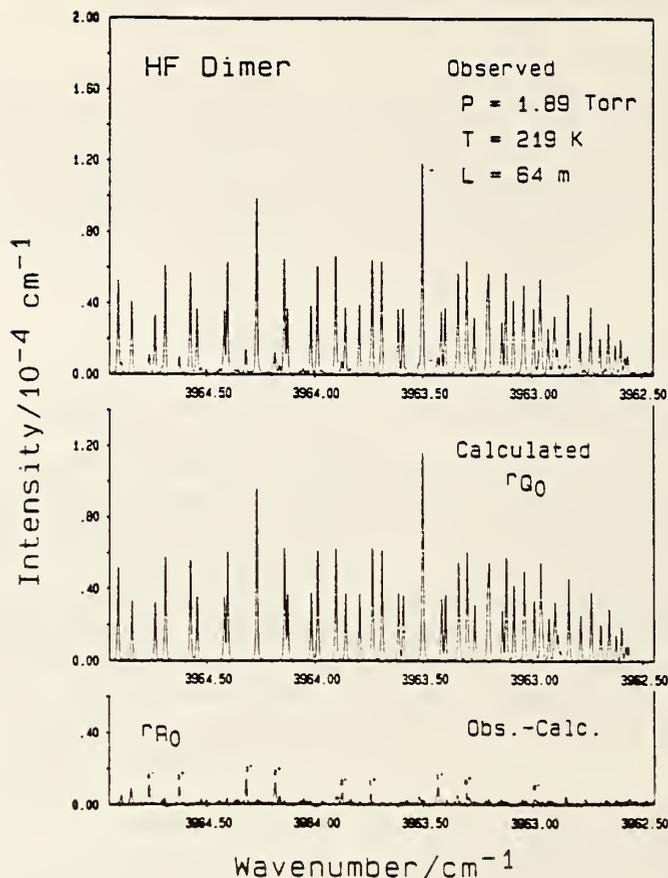


Fig. 2.6. Observed, calculated and residual spectra of the rQ_0 subbranch of the ν_1 band of the HF dimer.

The spectral intensities can be related to the dimer concentration n_D , and partition function, Q_D , and the transition moment, $\langle \mu_1 \rangle_D$, for the band component measured using standard formulae. In turn, n_D and Q_D can be expressed in terms of the monomer concentration, n_M , and partition function, Q_M , and the zero-point dissociation energy, D_0 , under thermal equilibrium by

$$K_{eq} = n_D / (n_M)^2 = (Q_D / Q_M^2) e^{D_0/kT} .$$

Since n_M is measured from the pressure assuming negligible polymerization and Q_M can be calculated trivially for a diatomic molecule, the only unknowns in the problem are D_0 and the transition moment for the dimer. Recent *ab initio* calculations have shown that the bond transition moment for the outer hydrogen is only ~10% enhanced over that of the monomer, which is known quite accurately from our recent measurements of the

absolute intensities of the monomers. Thus we need only to project the value of this moment onto the b-axis of the dimer to relate it to the $\langle \mu_1 \rangle_b$ observed.

We obtain zero-point dissociation energies for the HF and HCl dimers of $D_0 = 1038 (+43, -34) \text{ cm}^{-1}$ and $431 (\pm 22) \text{ cm}^{-1}$ respectively. Estimates of the zero-point energies of the low frequency intermolecular vibrations enable us to obtain the well depths and the equilibrium dissociation energies, $D_e = 1595 (+103, -94) \text{ cm}^{-1}$ for $(\text{HF})_2$ and $794 (\pm 86) \text{ cm}^{-1}$ for $(\text{HCl})_2$ for comparison to ab initio and model calculations for these complexes.

2. Rotational Predissociation and Libration in the Infrared Spectrum of Ar-HCl

(B. J. Howard and A. S. Pine)

Fully-resolved rotational structure in the high-frequency vibrational region of the Ar-HCl van der Waals complex has been recorded under thermal equilibrium conditions at $T=127 \text{ K}$ with a tunable difference-frequency laser. Both the fundamental H-Cl stretch and its combination with the low-frequency large-amplitude bend (libration) have been observed with comparable intensities. The fundamental H-Cl stretch gives rise to a parallel-type band in the null gap of HCl as shown in Figure 2.7. The assigned Ar-HCl spectrum is indicated in the calculated trace below the

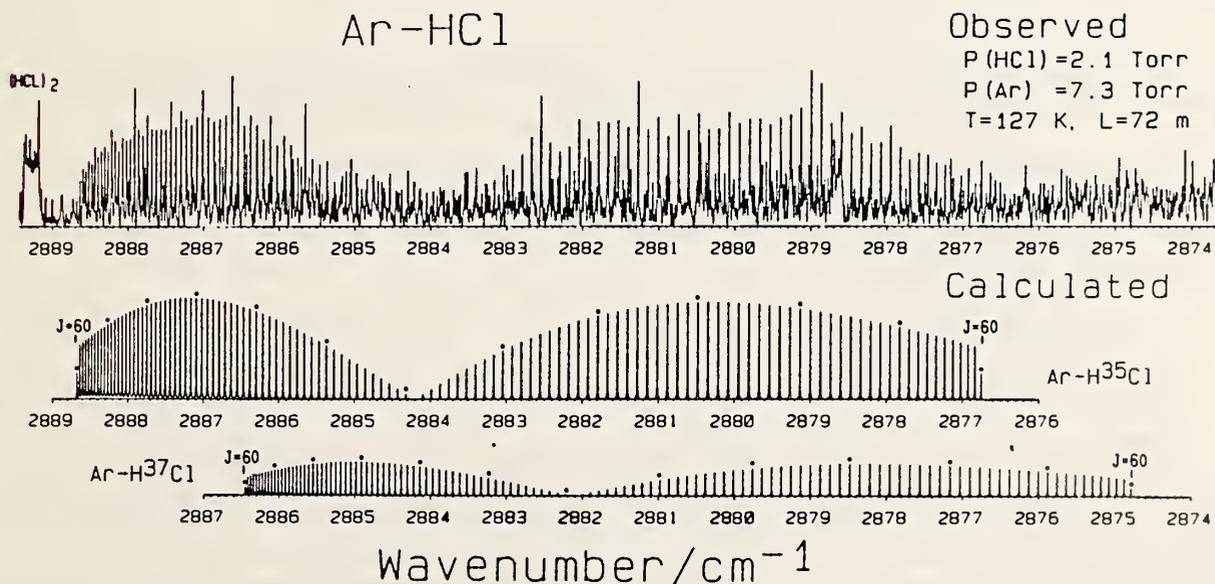


Fig. 2.7. Observed and calculated spectra of the ν_1 fundamental H-Cl stretching band of Ar-HCl.

observed spectrum which is unavoidably contaminated by HCl dimer structure (known from previous work) and hot bands. Both Cl isotopes contribute in their natural abundance. The abrupt cutoff of the spectrum at $J = 60$ arises from rotational predissociation as the rotational energy exceeds the binding energy and may tunnel through the top of the centrifugal barrier. The rotational eigenvalues and predissociation have been modeled with a one-dimensional radial potential of the Maitland-Smith form to give a zero-point dissociation energy of $D_0 = 114.7 (\pm 1.0) \text{ cm}^{-1}$ and a van der Waals stretching frequency of $\nu_3 = 31.3 (\pm 1.0) \text{ cm}^{-1}$. These values are in good agreement with empirical models based on precise microwave measurements near the minimum in the potential well, but disagree seriously with prior estimates based on the temperature dependence of the low resolution infrared spectrum. The rotational constants in the ground and excited H-Cl stretch vibrations yield a measure of the extension of the center-of-mass separation due to the motion of the proton. The red shift of the Ar-HCl spectrum from the isolated HCl monomer implies a stronger van der Waals attraction upon excitation of the H-Cl stretch.

The combination band of the H-Cl stretch, ν_1 , with the van der Waals band, ν_2 , is shown in Figure 2.8. It is a perpendicular-type band (Π - Σ) of anomalously high intensity transferred from the fundamental stretch by the strong modulation due to the wide librational motion. The blue shift from the fundamental band is about 34 cm^{-1} corresponding to the frequency of the bending mode. The rotational constants yield the extreme shortening of the van der Waals bond length upon bending the molecule, and they give the ℓ -doubling constant $q_1 = B_Q - B_R = + 34.2 (\pm 0.2) \text{ MHz}$ arising from Coriolis perturbations from nearby states with Σ -symmetry. These measurements should lead to improved estimates of the anisotropy of the potential and its dynamical behavior.

We have also obtained preliminary assignments of hot bands arising from ν_3 , the van der Waals stretching mode, in the fundamental band region of Ar-HCl. This gives us further information about the intermolecular potential and about interactions between the low frequency modes. Spectra have also been recorded for other rare gas (Ne, Kr, Xe)-HCl complexes to obtain the trends of the van der Waals potential with regard to atomic mass and polarizability.

3. Study of Hydrogen-bonded complexes in the Gas Phase Using Fourier Transform Spectroscopy

(B. A. Wofford, J. W. Bevan, W. B. Olson, and W. J. Lafferty)

During the past year, we have had a very fruitful collaboration with Professor John Bevan and B. A. Woffard from the Chemistry Department of Texas A&M University. From designs developed by W. B. Olson (see Section 3.1), Prof. Bevan and his co-workers have built a long-path absorption cell which can be cooled to ca. -100° C . At low temperatures, the hydrogen-bonded complexes are present at higher concentrations. The long absorption path (up to 64 meters) serves to enhance the instrumental

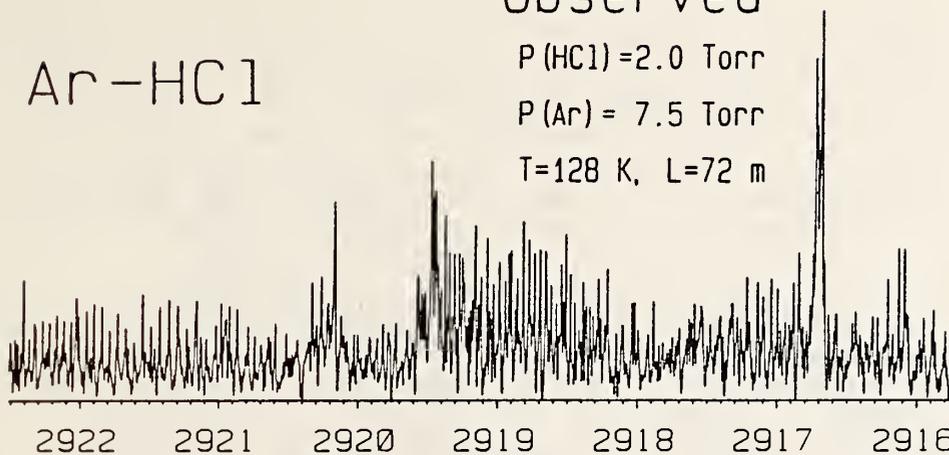
Ar-HCl

Observed

P(HCl) = 2.0 Torr

P(Ar) = 7.5 Torr

T = 128 K, L = 72 m



Calculated

Combination Band

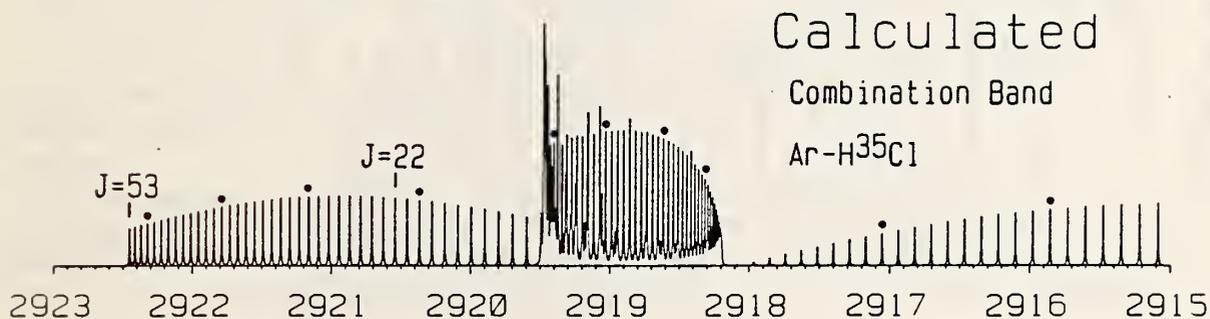
Ar-H³⁵ClWavenumber/cm⁻¹

Fig. 2.8. Observed and calculated spectra of the $\nu_1 + \nu_2$ stretch-bend combination band of Ar-HCl.

sensitivity. This cell has been coupled into the NBS BOMEM spectrometer and used to study a number of rotation-vibration bands of several hydrogen-bonded complexes including HCN...HF, HCN...HCN, and HCN...HCl. At this point the work on the HCN-HF complex is most complete. Five of the absorption bands of this complex have been observed, and many of the individual line transitions assigned. These bands arise from the C-H stretching fundamental and its overtone, the CN stretching vibration, the internal HCN bending vibration, as well as the bending vibration in which one end of the complex twists with respect to the other end. The latter vibration is unique to the hydrogen-bonded complex, and is not overlapped by lines from either HCN or HF. The Q-branch of this band is shown in Figure 2.9.

The dissociation energy for these weakly bound complexes is, of course, rather low; e.g., for HCN...HF, D_0 is about 1600 cm^{-1} . Thus many of the molecular vibrations lie above the dissociation limit, and high resolution spectroscopy, in addition to providing information on the energy levels of hydrogen-bonded molecules, allows one to approximate the life time of molecules in energy levels above this limit. The width of a

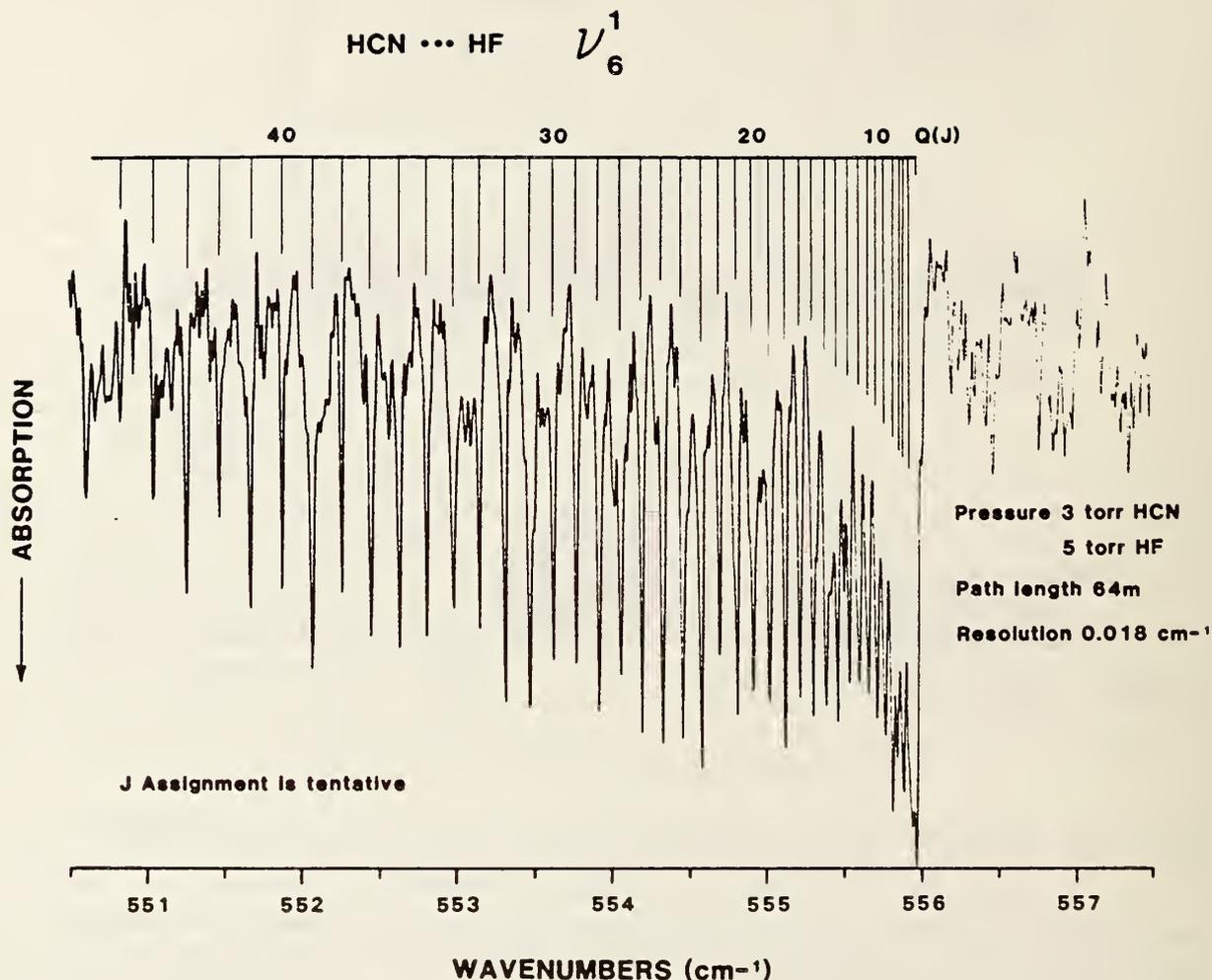


Fig. 2.9 A Q-branch of the high-frequency bending vibration, ν_6^1 , of the hydrogen bonded complex HCN...HF recorded at a temperature of -50°C . Despite the unusually high stability of this complex, a path length of 64 meters was required to obtain the spectrum with a reasonable signal-to-noise level. This vibration is unique to the hydrogen-bonded complex and there is no overlapping from lines of the parent species.

ro-vibrational line is inversely proportional to the lifetime of the molecule in the upper state of the transition. The lines of several bands of the HCN...HF molecule were found to be considerably broader than the instrumental resolution, and, therefore, lifetimes of several vibrational states could be estimated. For example, the lines of the C-H stretching vibration at 3310 cm^{-1} were not broadened and one can estimate that the molecular lifetime of this state is at least 10^{-8} sec. The overtone of

this vibration at 6517 cm^{-1} is slightly broadened, and the lifetime of this level is on the order of 2.4 ns. The CN group is directly involved in the hydrogen bond, and the lines of the CN stretching vibration at 2121 cm^{-1} are very broad. The lifetime of molecules in this state is about 2.56 ns. Not surprisingly the lower frequency bands, which have vibrational frequencies below D_0 , have sharp lines, and only an upper limit estimate of the lifetimes can be made for the upper states of these vibrations.

These studies will shortly be extended to the far infrared region to study the rest of the vibrational transitions unique to the complex.

4. Pulsed Beam Fabry-Perot Cavity Fourier Transform Microwave Spectrometer

(R. D. Suenram and F. J. Lovas)

The construction of a pulsed beam Fabry-Perot cavity Fourier transform microwave spectrometer was briefly described in last year's annual report.

The major emphasis of our efforts in the past year have involved testing the new spectrometer with a number of previously observed hydrogen bonded species and van der Waals complexes to obtain experience in the operation of the instrument and optimization of the detected signals.

Two areas in which the instrument excels are high sensitivity and high resolution. In order to assess the sensitivity a 2% mixture of OCS in argon was prepared and the 1-0 transition of the various isotopes of OCS studied in natural abundance. Figure 2.10 shows the 1-0 transition of

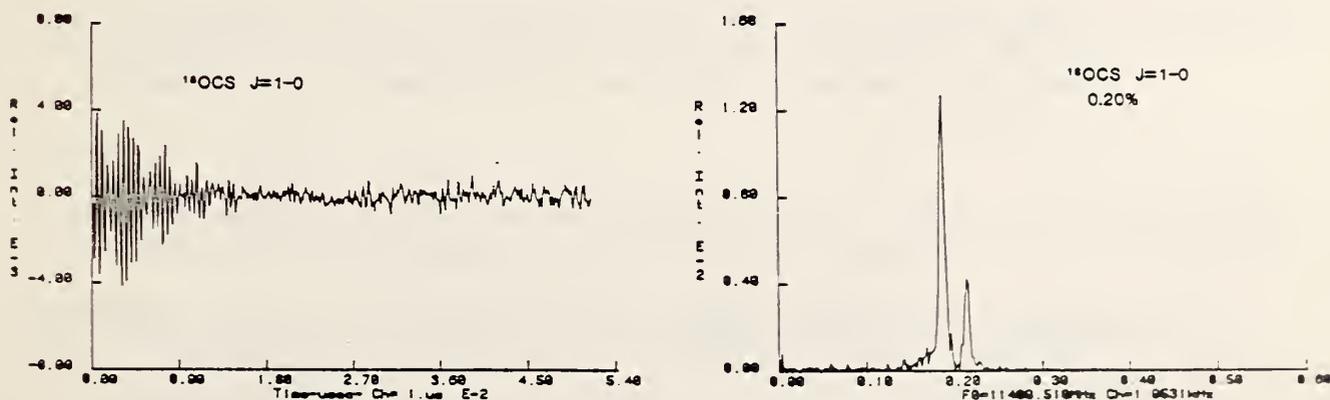


Fig. 2.10. Rotational spectrum of the $J=1-0$ transition of ^{18}OCS . Left: time domain spectrum obtained with 500 nozzle pulses. Right: frequency domain spectrum; Fourier transform of spectrum shown on the left. The signals were observed with a 2% mixture of OCS in argon.

^{18}OCS which occurs in 0.21% natural abundance. The trace is a summation of signals for 500 nozzle pulses but this signal is easily observable on a single pulse. The weakest signal observable was that of $^{18}\text{OC}^{34}\text{S}$ which occurs in 0.0086% natural abundance. This signal was observed with a summation of 2500 pulses. The ^{18}OCS signal, which is observable on a single pulse, corresponds to approximately 10^{13} molecules per pulse. Several improvements of the instrument are planned for the next year which should easily increase the sensitivity by an order of magnitude.

The high resolution aspect is shown in Figure 2.11 where the 1-0 transition of $(\text{H}_2\text{O})_2$ is shown. The four individual peaks arise from the spin-spin hyperfine interaction associated with the H nuclei. The splittings are

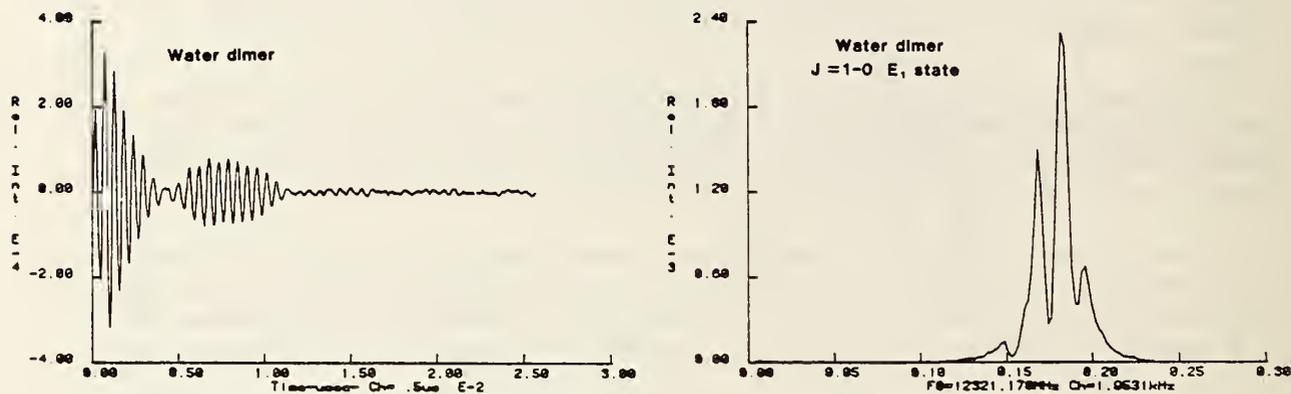


Fig. 2.11. Time domain (left) and frequency domain (right) spectrum of the $J=1-0$, E-state transition of the water dimer at $\nu = 12321.0$ MHz. The frequency splittings (right side) are approximately 16-20 kHz.

on the order of 16-20kHz. We have found that with certain nozzle/pressure configurations we can obtain line widths on the order of 8-12kHz (FWHM).

The following two reports (D.5 and D.6) describe new results obtained for Ar...acrylonitrile and Kr...OCS.

5. Microwave Study of the Ar...Acrylonitrile van der Waals Complex (F. J. Lovas and R. D. Suenram)

The van der Waals complex of argon with acrylonitrile ($\text{Ar}\dots\text{CH}_2\text{CHCN}$) has been observed with the pulsed beam instrument. This particular complex was chosen as the first new molecular species for the new instrument for a variety of reasons. First the dipole moment is large so

the spectra should be quite intense. Second, the ^{14}N nucleus provides characteristic quadrupole splittings which should be predictable and thus useful for the assignments of the transitions. Third, the species is large enough so that the transition density is fairly high (a strong transition every 100 MHz or so) which should enable several transitions to be found without a great deal of searching. Last, there are a variety of sites where the Ar could bind to acrylonitrile. It will be extremely interesting to see which conformation is the dominant one.

Two discrete sets of rotational transitions have been observed. For one set, the energy levels lie approximately $0.5 - 1.0 \text{ cm}^{-1}$ higher in energy than the other set. More than thirty transitions have been observed and fitted for the low energy (ground state) and over twenty transitions have been measured and fitted for the higher energy (vibrational) state. Each of these transitions is split by the nuclear quadrupole interaction associated with the ^{14}N nucleus.

From a rotational analysis of the transitions, and analysis of the nuclear quadrupole hyperfine structure, the molecule appears to favor one of the two possible structures shown in Figure 2.12. Further work with deuterium isotope labeling will have to be done in order to discriminate which is the true structure. Our intuitive feeling is that the "inside" structure is probably the correct one, since the "outside" structure requires an Ar...H distance that is shorter than for the normal van der Waals radii of the atoms. In either case, the Ar atom lies at an angle of approximately 40° with respect to the plane of the acrylonitrile subunit.

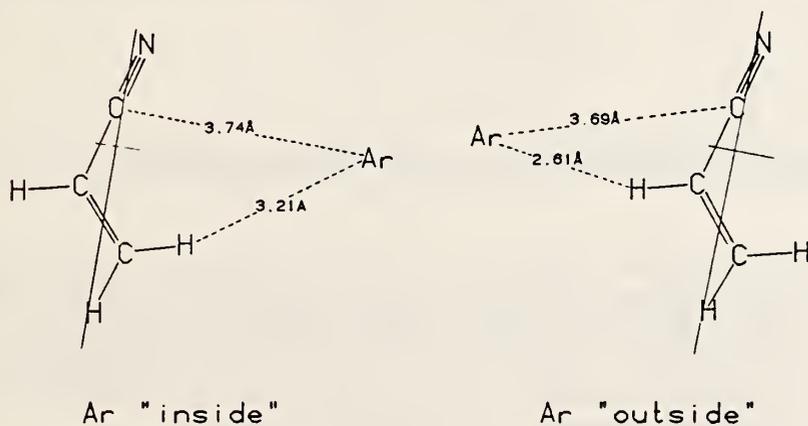


Fig. 2.12. Favored structures for the argon-acrylonitrile van der Waals complex.

6. Microwave Study of the Kr...OCS van der Waals Complex (F. J. Lovas and R. D. Suenram)

During Dr. B. J. Howard's visit at NBS the possibility was discussed of looking for the microwave spectrum of neon and krypton bonded to carbonyl sulfide. Work in the infrared region in his laboratory at Oxford

University had provided approximate values for the rotational constants of both Ne...OCS and Kr...OCS in the ground state and $v=1$ of the CO stretching vibration. Accurate values for the rotational constants of these species in the ground state, obtained by microwave spectroscopy, could be used in the analysis of the infrared spectra to obtain very precise values for the upper state constants.

Some time was spent searching for Ne...OCS but no transitions were found. Transitions of Kr...OCS on the other hand were readily observed. Subsequent microwave-infrared double resonance work on Ne...OCS in Oxford indicated that the preliminary rotational constants were much more uncertain than originally thought; as a result, we never searched the proper region to detect a transition of Ne...OCS.

For Kr...OCS transitions for four isotopes (^{84}Kr , 57%; ^{86}Kr , 17%; ^{82}Kr , 11%; and ^{83}Kr , 11%) have been observed and analyzed. The structure of the complex is planar and T-shaped, similar to Ar...OCS (see Fig 2.13). One note of interest is that nuclear hyperfine structure has been observed

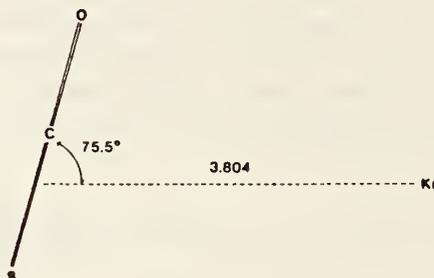


Fig. 2.13. Structure of the Kr...OCS van der Waals complex

on ^{83}Kr ...OCS transitions (see Figure 2.14). The ^{83}Kr atom has a nuclear spin of $9/2$ and thus, a nuclear electric quadrupole moment. Although the electron orbitals of the atom are spherically symmetric, these are distorted in the van der Waals complex and cause hyperfine interactions. Analysis of this hyperfine structure should enable us to study the distortion of the spherical symmetry upon complexation.

Quite recently we have incorporated a set of Stark plates into the spectrometer for dipole moment measurements. These were placed ~ 25 cm apart, so that the cavity Q would not be changed appreciably, and provide $\Delta M_J = \pm 1$ selection rules. Analysis is in progress on the Stark effect of Kr...OCS. Figure 2.15 shows three Stark components of the $3_{12}-2_{02}$ transition.

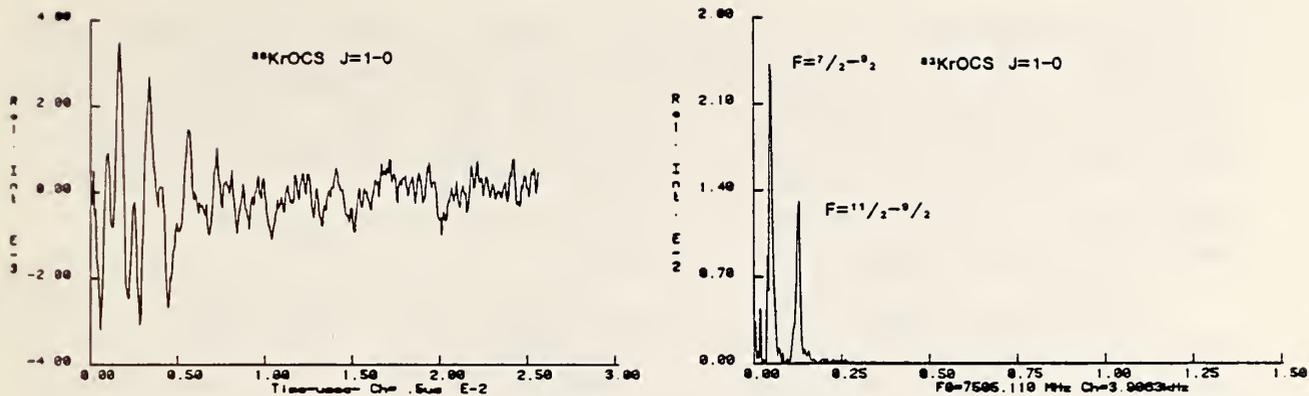


Fig. 2.14. Time domain (left) and frequency domain (right) spectrum of the $J=1-0$ rotational transition in $^{83}\text{Kr}.. \text{OCS}$ at 7505.11 MHz. The $\Delta F=0$ transition is not shown in the figure; it was found at 7504.6 MHz.

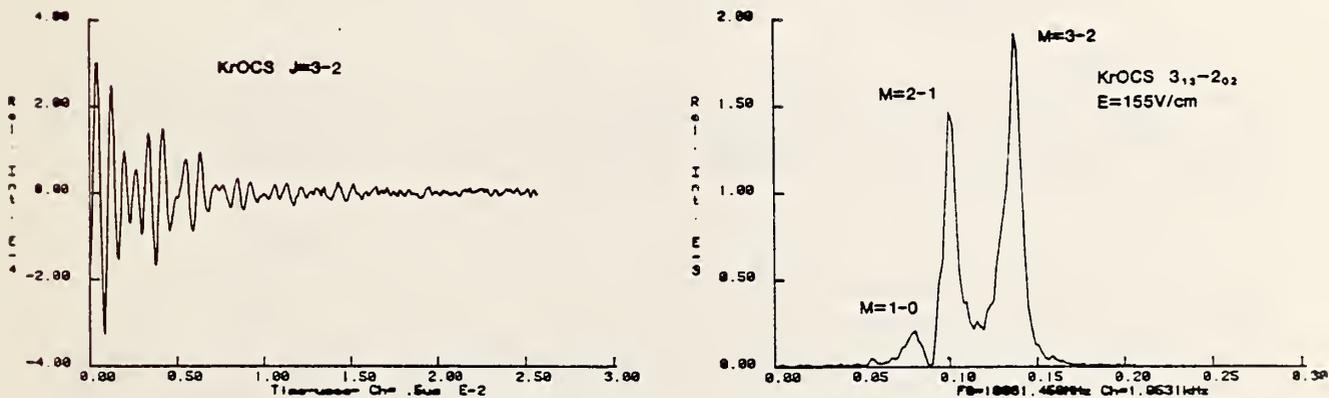


Fig. 2.15. Time domain (left) and frequency domain (right) Stark spectrum of the $J=3-2$ line of $\text{Kr}.. \text{OCS}$ obtained with a field of 155V/cm.

7. A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer (J. T. Hougen)

When more than one large amplitude vibrational motion is present in a molecule, it is often not possible to define a global internal-axis-method (IAM) coordinate system and set of basis functions. In the present work, a method is presented for extending the IAM treatment to tunneling problems in such cases, using as an illustration a model for the water dimer with three large amplitude vibrational coordinates. The method

involves the construction of two different sets of local IAM-like coordinate systems. The first of these contains n coordinate systems, one for the small neighborhood surrounding each of the n equilibrium frameworks. The second contains on the order of $n^2/2$ coordinate systems, one for each feasible tunneling path between each pair of frameworks. Basis functions written in the second set of local IAM-like coordinates are used to determine the complex phase factors associated in this method with tunneling matrix elements of the phenomenological rotational Hamiltonian in the high barrier limit.

These phase factors govern the way in which the various real tunneling frequencies in the molecule constructively and/or destructively interfere in the Hamiltonian matrix elements and final energy expressions. Various mathematical approximations are involved in using the local IAM-like basis sets to obtain matrix elements; the full extent of the adverse effects of these approximations will not be known until an attempt to fit experimental data is carried out.

E. General Spectroscopy and Theory

1. Efficient Sampling Systems for the Fourier Transform Spectrometer (Wm. Bruce Olson)

A transfer optics system has been designed, and constructed for the coolable White cell made from our design by Prof. J. Bevan at Texas A&M Univ. Prof. Bevan also had made an evacuable chamber for the transfer optics. The utility of this system for use in the far infrared has been demonstrated.

A preliminary optical design using a single concave mirror has also been worked out for the transfer optics to couple the BOMEM FTIR spectrometer to an existing heat pipe for use in the far infrared. An important feature of this and the previous system is that a single concave mirror is used to accomplish two objectives. An image of the input aperture of the FTIR is placed at the entrance of the cell, and an image of the beamsplitter is placed on, and exactly fills, a back mirror of the White cell, or exactly fills the exit aperture of the heat pipe. Under these conditions a simple thin window, but no field lens is required at the input of the sample cell, in order to pass the maximum possible signal radiation, and the problem of a suitable optical material for a field lens is eliminated.

2. Diode Laser Measurements on Unstable Diatomic Molecular Species (A. G. Maki, G. A. Thompson, and A. Weber)

In an effort to study molecular species that are unstable in the gas phase under ordinary conditions, we have used a high temperature technique to measure the infrared spectrum of GeO, LiI, and LiD in the gas phase. These are the first resolved gas phase infrared measurements to be made of these species although the electronic and microwave spectra have been studied in the gas phase. The extent of the measurements is indicated in

Figure 2.16. which gives the range of vibrational and rotational levels covered by these measurements for $^{74}\text{Ge}^{16}\text{O}$ and $^7\text{Li}^{127}\text{I}$. All five isotopic germanium species of GeO have been measured in natural abundance as can be seen in Figure 2.17 which shows a portion of the measured spectrum. So far only the most abundant isotopic species of LiI and LiD have been observed.

To analyze measurements of this sort we have developed a non-linear least-squares fitting program to determine a set of Dunham potential coefficients that define the lower part of the potential well for the molecules under study. Most other workers use such measurements to

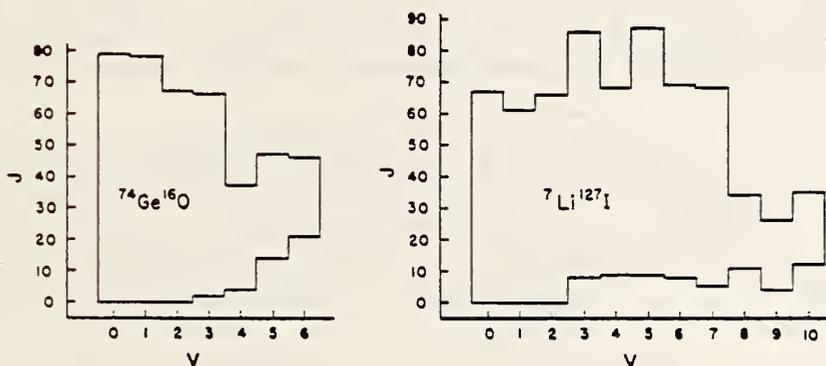


Fig. 2.16. Extent of data base for rotation-vibrational bands of GeO (left) and LiI (right) determined from infrared diode laser spectra. In these displays the vibrational states are depicted in strips one unit wide, and centered about the integral value of the vibrational quantum number v .

determine directly a set of ro-vibrational constants that ignores the underlying concept of a potential well and therefore may be in conflict with any reasonable potential function.

We believe that a more useful analysis uses the data to determine the potential function and then uses the potential function to determine a consistent set of ro-vibrational constants.

The problem with using ro-vibrational constants for calculations that represent an extrapolation outside the range of observations is that the constants are usually determined without restraining them to a physically meaningful model. Our way of determining the ro-vibrational constants gives them greater reliability for calculating levels and transitions outside the range of measurements because the underlying concept of a potential function restrains many of the higher order ro-vibrational constants to physically realistic values.

In the case of GeO all five measured isotopic species have been fit to a single potential function which can be used to calculate the observed transitions with an rms deviation of 17 MHz which we believe represents the accuracy of the measurements.

GeO

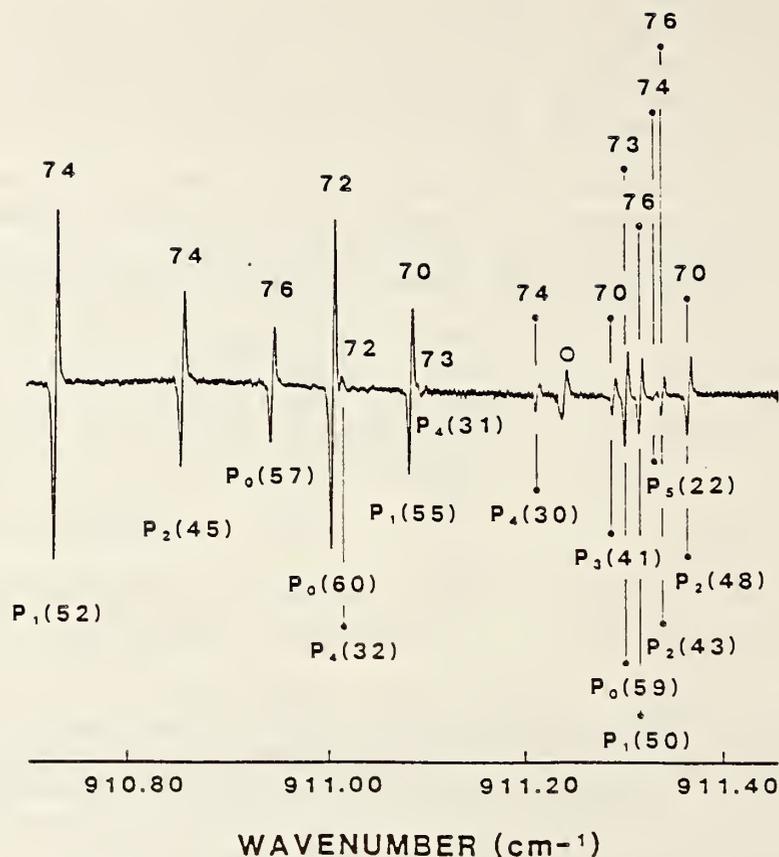


Fig. 2.17 Portion of the infrared diode laser absorption spectrum of GeO. Numbers in the top part identify the Ge-isotope. The assignments of the individual rotation-vibrations are given in the lower half; the subscripts label the vibrational state. The line marked with an open circle is due to an impurity.

The work on LiD is not yet finished. In the coming year we expect to also observe the spectrum of ⁶LiD.

We have also been measuring transition frequencies and relative intensities for ClO. Since those measurements are of interest for atmospheric studies, they are described in section C on studies related to atmospheric chemistry.

3. Fourier Transform Raman Spectroscopy of H₂ and D₂ in Flames
(A. Weber and D. A. Jennings)

The successful demonstration of the use of a Fourier transform spectrometer to record Raman spectra of gases under high resolution was reported in last year's Annual Report. Together with Dr. J. W. Brault of

the National Solar Observatory located at Kitt Peak, AZ, work on the high temperature spectra of H_2 and D_2 has been done with the 1-meter FTS instrument of the McMath Solar telescope at Kitt Peak.

Laboratory spectra of high rotational transitions in H_2 are important in astrophysics because they may be observable in hot stellar and interstellar sources, and have already been seen in quadrupole emission from the Orion molecular cloud.¹ The Orion emission lines are characteristic of an $\sim 2000K$ rotational temperature. Infrared spectra of H_2 and D_2 at high temperatures are difficult to obtain in the laboratory because path lengths of hundreds of meters are necessary to observe the quadrupole absorption. Vibration-rotation coefficients obtained from room temperature spectra cannot be extrapolated to the high- J lines observed in Orion to within the accuracies of the astronomical measurements.

Prompted by these considerations, we have recorded Raman spectra of high temperature molecular hydrogen and deuterium using a Fourier transform spectrometer. A diffusion flame source burning H_2 or D_2 in air was placed at the focal point of a multi-pass mirror system.² Figure 2.18 shows the pure rotation spectrum of D_2 obtained in this manner; the room temperature spectrum is shown for comparison.

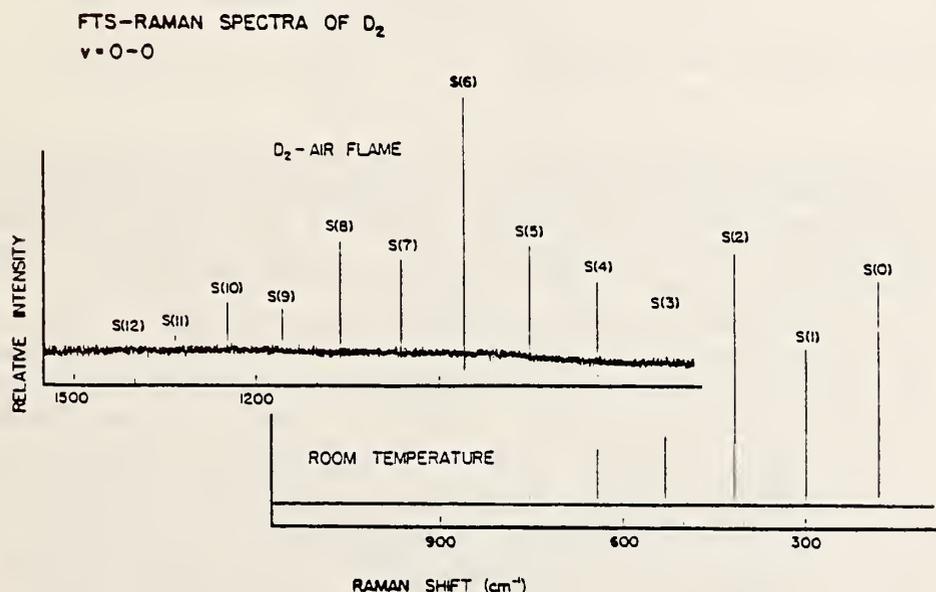


Fig. 2.18. Pure Rotational Raman Spectra of D_2 for a diffusion flame in air (top) and a stagnant gas at room temperature (bottom).

As expected the higher temperature spectrum (flame) shifts the intensity distribution toward higher J -values, with $S(12)$ being the highest transition observed. The noisy and varying background in the high temperature spectrum is caused by the flame itself. Similar observations were made on H_2 for which both the $\nu=0-0$ and $\nu=1-0$ spectra were recorded

to S(7) ($v=0-0$) and Q(5) ($v=1-0$) in the flame spectra. The data bases for the $v=0-0$ and $v=1-0$ transition of H_2 and D_2 have been extended through the inclusion of the Raman flame data. Improved ground state constants for D_2 are listed in Table 2.2.

Table 2.2 Ground State Parameters of D_2 (cm^{-1}).

Constant	Flame + Room Temp.	Room Temp. Only
B_0	29.91371(44)	29.91439(40)
D_0	0.011527(22)	0.011599(19)
H_0	$6.84(40) \times 10^{-6}$	$9.10(24) \times 10^{-6}$
L_0	$-1.11(29) \times 10^{-8}$	---
M_0	$3.09(69) \times 10^{-11}$	---
ΔE_m	$\Delta E_6(J)$	$\Delta E_4(J)$

- (1) R. F. Knacke and E. T. Young, Ap. J. (Letters) 249, L65 (1981).
 (2) R. W. Hill, A. J. Mulac, and C. E. Hackett, Appl. Opt. 16, 2004 (1977).

4. Infrared Spectrum of Cyanogen (A. Weber, W. J. Lafferty, and W. B. Olson)

Previous work on the high resolution infrared spectrum on C_2H_2 was described in last year's Annual Report. In that work the ν_3 and ν_5^1 fundamental bands were recorded with the BOMED DA3.002 Fourier transform spectrometer using only a 20cm absorption path. The ν_3 band was recorded at a pressure of 5 torr which caused noticeable pressure broadening of the lines. In the present work a White cell (maximum path length 20 m) was employed to re-record the ν_3 band system, as well as to obtain spectra of the $\nu_1+\nu_5^1$, $\nu_3+\nu_4^1$, $\nu_1-\nu_5^1$, and $\nu_2-\nu_5^1$ combination and difference bands at an apodized resolution of 0.004 cm^{-1} . Because of the low lying fundamentals ν_4^1 and ν_5^1 these bands are accompanied by numerous hot bands which complicate the assignment process, but which yield precise values for the energy levels of the lower states. Figure 2.19 shows the region of the ν_3 band using a path length of 2.25m and a gas pressure of 1.51 torr. The OCS is present as an impurity in the gas sample. The $\nu_1-\nu_5^1$ band plus its hot bands is now present with a good signal to noise ratio. In the previous spectra only its Q-branch was visible, with very poor signal to noise. Similarly the ν_3 and $\nu_3+\nu_5^1-\nu_5^1$ bands of the isotopic species $^{13}C^{12}CN_2$, present in natural abundance, are observed in the present spectra. Extensive structure was observed in the $\nu_1+\nu_5^1$ and $\nu_3+\nu_4^1$ combination bands. The $\nu_1+\nu_5^1$ band contains an heretofore unreported perturbation. The $\nu_2-\nu_5^1$ band system near 610 cm^{-1} was recorded for the first time under high resolution. This band is weak and, owing to the use

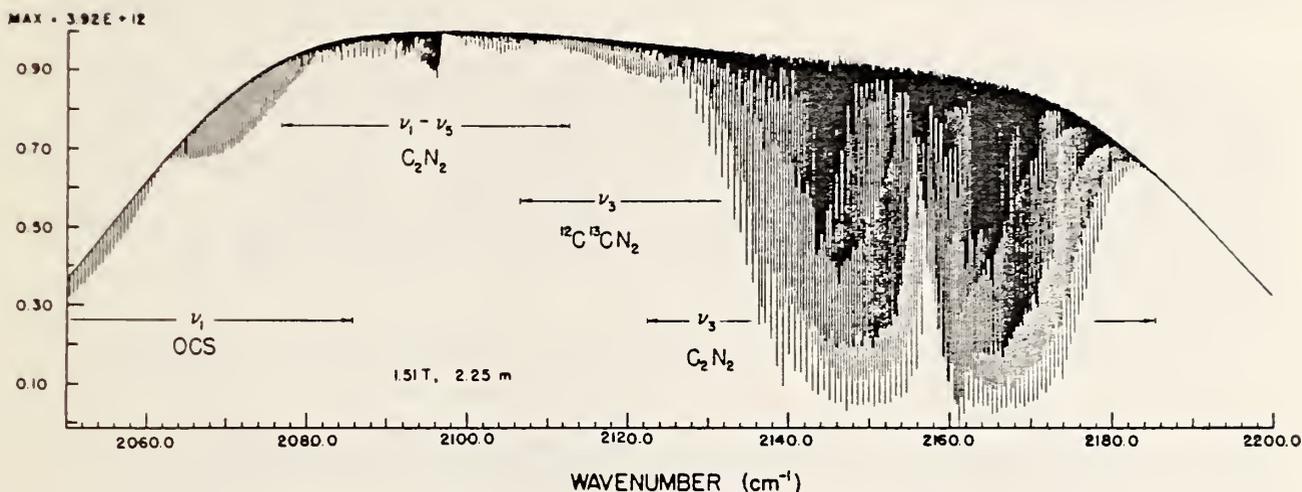


Fig. 2.19 Region of the ν_3 -band of C_2N_2 recorded with the BOMEM DA3.002 Fourier transform spectrometer at a (opodized) resolution of 0.004 cm^{-1} . The spectrum is the result of 64 scans taken one a time of 5 h. 20 m.

of the less sensitive HgCdTe detector, a rather high pressure of 39.9 torr was necessary for its observation. The analyses of the various bands are well under way though the perturbation in the $\nu_1 + \nu_5$ band remains to be identified. The upper state of the $\nu_3 + \nu_4^{\pm 1} + \nu_5^{\mp 1} - \nu_5^{\pm 1}$ band is split into a Σ_g^+ and a Σ_g^- component, both of which have been identified. This is only the second known case (the other being C_2H_2) in which a $\Sigma_g^- - \Pi_u$ transition has been observed and identified. Besides improved values for the constants of the ν_3 , $\nu_1 + \nu_5^1$ and $\nu_3 + \nu_4^1$ band systems new results have been obtained for the $\nu_2 - \nu_5^1$ system as well as for the ground state of $^{13}C^{12}CN_2$. The extensive data base of the combination and difference bands has also enabled us to obtain more accurate values for the frequencies of the ν_1 and ν_2 fundamentals. These fundamentals are of species Σ_g^+ and are thus only observable in the Raman spectrum. The present results are: $\nu_1 = 2330.4847(5)$ and $\nu_2 = 845.5965(15)\text{ cm}^{-1}$. They are more accurate than the Raman results and will serve in the determination of a more accurate force field of cyanogen.

5. Fourier Transform IR Spectra of Monodeuterosilane
(Wm. B. Olson and R. W. Lovejoy)

Assignments in the vibrational bands ν_6 , ν_3 , ν_5 , ν_2 and $2\nu_6$ have been greatly extended since last years report. Identification of perturbation

allowed transitions with high values of the K quantum number in ν_3 and ν_5 has enabled for the first time a direct experimental determination of D_O^K and a smaller error (by a factor of 150) than that of our previous determination[†] of A_0 .

We were unaware at the time of last year's report that another group of workers in Europe had taken the same spectra and had nearly completed the assignments. This group is headed by Prof. H. Bürger, Universität-Gesamthochschule, Wuppertal, West Germany. Since that group had access to computer software for fitting the three bending fundamentals, we (by agreement with Prof. Burger) abandoned work on these and have concentrated on the analysis of the ν_2 and $2\nu_6$ parallel and perpendicular bands.

The extreme weakness of the perpendicular component of $2\nu_6$ leads to no observable transitions in this band except those whose intensities are obtained by perturbations with ν_2 and the parallel component of $2\nu_6$. Several perturbations are observed, and about twenty transitions of $2\nu_6$ have been assigned, but we do not yet have enough data for a reasonably good analysis, and the slow assignment and checking process is still in progress.

(1) Olson, W. B., and Lovejoy, R. W., J. Mol. Spectrosc. 66, 314-330 (1977).

6. Far Infrared Spectrum of the Torsional Band of Hydrazine (N. Ohashi, W. J. Lafferty, and W. B. Olson)

Hydrazine has two large amplitude motions, an NH_2 wagging vibration (similar to the umbrella motion in NH_3), and the torsional vibration. Only recently have theoretical methods become available to treat the observed spectra[†], and they have been successfully used to fit the pure rotational microwave spectrum. While the ground state has large splittings arising from the inversion motion, torsional splittings in the ground state are quite small.

We have studied the torsional vibration of N_2H_4 where the torsional splitting contributions will be much larger than in the ground state spectrum in order to further test the theory, as well as to attempt to determine the barrier to internal rotation. The center of this band is at 376 cm^{-1} . It is a b-type band, and since the A rotational constant of the molecule is large, it covers a large portion of the spectrum from about 300 cm^{-1} to 450 cm^{-1} . The spectrum was recorded with the NBS BOMEM FTS spectrometer at a resolution of about 0.01 cm^{-1} .

Although the spectrum is somewhat complex due to the fact that each rovibrational transition is split into either four or six components (depending upon whether the lower state K of the transition is even or

odd), and also because of overlapping by "hot band" transitions, we have been able to make a very satisfactory line assignment with the aid of combination differences calculated from ground state constants obtained in a recent microwave study.²

The assigned transitions were combined with the observed microwave data and fit using Hougen's Hamiltonian.¹ The inversion and torsional splittings of both the ground and torsional states were obtained. As expected, the torsional splitting in the vibrational state (1824 Mhz) was found to be many-fold larger than the torsional splitting in the ground state (5.8 MHz). However, a surprisingly large vibrational change in the inversion splitting was found. This splitting was determined to be 7976 MHz in the torsional state as compared to a splitting in the ground state of 16040 MHz. The height of the barrier to internal rotation was estimated to be $2100 \pm 50 \text{ cm}^{-1}$.

- (1) J. T. Hougen, J. Mol. Spectrosc. 89, 296 (1981).
- (2) S. Tsunekawa, T. Kojima and J. T. Hougen, J. Mol. Spectrosc. 95, 133 (1982).

7. The Torsional-Wagging Tunneling Problem and the Torsional-Wagging-Rotational Problem in Hydrazine (N. Ohashi and J. T. Hougen)

Results derived previously for the rotational levels of the eight-framework and three-large-amplitude vibrational problem in N_2H_4 , using a tunneling formalism based on a treatment of the vibration-rotation problem as a whole, were rederived in a much simpler fashion, using a tunneling formalism based on separate treatment of the vibrational and rotational problems. The present formalism is thus much more akin to the usual vibration-rotation formalism, and the origins of the various contributions to the vibration-rotation energy levels can be understood relatively easily. It is convenient here, as earlier, to make extensive use of permutation-inversion and extended-group (double-group) ideas, but it is necessary in the present treatment to consider tunneling between 16 minima in molecular coordinate space, i.e. between a number of minima which is twice the number of nonsuperimposable molecular frameworks that can actually be constructed for N_2H_4 .

8. The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric-Top High-Barrier Internal Rotor Molecules like $\text{H}_3\text{C-SiH}_3$ (J. T. Hougen)

The m -fold extended group $G_{18}^{(m)}$, corresponding to the permutation-inversion group G_{18} for molecules like $\text{H}_3\text{C-SiH}_3$, has been obtained. In this extended group, m is the smallest integer for which $m\rho$ is also an "integer," where ρ is the usual ratio of the moment of inertia of the top about the rotational A axis to the moment of inertia of the molecule about the A axis. The extended group has $18m$ elements, divided

into $(9m+3)/2$ or $(9m+6)/2$ classes, for odd and even values of m , respectively. Using this extended group, it is possible to assign definite symmetry species in an internal-axis-method (IAM) treatment to laboratory-fixed, molecule-fixed, top-fixed and frame-fixed projections of vector operators like the rotational angular momentum and the nuclear spin angular momenta. Thus, it is possible to express the spin-rotation and spin-spin contributions to the hyperfine interaction operator in terms of rotational angular momentum components, nuclear spin angular momentum components, and functions of the torsional angle, all of which have known symmetry species and selection rules in the IAM basis set. Using a hyperfine Hamiltonian constructed from these considerations, it is possible to understand the large variations in magnitude of some observed hyperfine couplings in recent molecular beam studies of symmetric top internal rotor molecules.

9. Improved Least Squares Determination of Potential Energy Surfaces from Spectroscopic Data
(C. Leubner and J. T. Hougen)

The value of a knowledge of potential energy surfaces for the understanding of the overall properties and behavior of a molecule can hardly be overestimated. With the exception of the simplest molecules, it can safely be stated that currently it is the observed spectrum that contains the most complete - albeit indirect - information on the molecular force field. As a consequence, much effort has been expended on the retrieval of potential energy surfaces from spectroscopic data.

Vidal and coworkers have shown in a number of applications that such a program - termed "Inverted Perturbation Approach (IPA)" and reviewed in (1) - can indeed be carried quite far in the diatomic case, where a number of problems are absent that become crucial in the polyatomic case. These qualitative differences preclude a straightforward, similarly successful, generalization of the IPA to the determination of potential energy surfaces. However, the main ingredients of the IPA have been used by the workers in the field of polyatomic molecules with more moderate results. Chen et al. (2) recently showed that none of the surfaces determined by these methods for the water molecule agrees with the observations to within spectroscopic accuracy.

However, it is possible to identify three promising areas for the improvement of the conventional approach. First of all, the variational character of the IPA can be combined with the necessarily variational calculation of the eigenvalues of the Schroedinger equation for a polyatomic molecule to give a very compactly formulated optimization problem, the solution of which would, in principle, immediately give the optimum potential energy surface corresponding to the measured energy eigenvalues in a least squares sense.

Secondly, this optimization problem involves as a crucial step a sufficiently accurate determination of the ro-vibrational eigenvalues of the Hamiltonian of the molecule under study. Chen and coworkers (2) have reported encouraging results with the conventional expansion of the eigenstates in products of "rotationless vibrational" wavefunctions and symmetric top functions. Alternatively, one could invoke so-called "distributed Gaussian bases", as recently introduced into the nuclear molecular problem by Hamilton and Light (3), which, after all, have proved superior to all other basis sets in the electronic molecular problem, where they are now exclusively used.

Thirdly, one requires a sufficiently flexible representation of the potential energy surface. As an improvement over the conventional Taylor series expansion in suitably chosen coordinates around the equilibrium point of the surface, we propose to supplement this by a Spline approximation (4) that adequately incorporates the full symmetry of the problem. The parameters of this Spline approximation are then to be optimized in a least squares sense with respect to the observed spectrum.

An investigation that focuses on these three areas of improvement is currently under way in collaboration with M. Wolfsberg of the Department of Chemistry, University of California, Irvine, CA.

- (1) C. R. Vidal: Accurate determination of potential energy curves (preprint) 1985.
 - (2) C.-L. Chen, B. Maessen, and M. Wolfsberg: Variational calculations of rotational-vibrational energy levels of water (preprint) 1985.
 - (3) I. P. Hamilton and J. C. Light: On distributed Gaussian bases for multi-dimensional vibrational problems (preprint) 1985.
 - (4) J. H. Ahlberg, E. N. Nilson, and J. L. Walsh: The Theory of Splines and their applications (Academic: New York 1967).
10. The Proper Choice of the Lagrangian for a Relativistic Particle in External Fields
(C. Leubner)

It is an unsatisfactory feature of the educational literature that renowned authors propose apparently conflicting prescriptions for the construction of an appropriate Lagrangian to describe the interaction of a relativistic point particle with external fields. The point where opinions sharply differ is whether, in the case where the independent parameter is to be the proper time of the particle, the equations of motion should be derived from Hamilton's principle by constrained or unconstrained variation. Therefore, it is shown that there exists a unifying point of view, which allows a consistent derivation of all these seemingly unrelated or even incompatible Lagrangians, which completely

clarifies their status and interrelations, and, moreover, provides a sound basis for discussing coherently a multitude of related issues that have emerged in the literature in an often obscure and even misconstrued manner. The results are to appear in the European Journal of Physics.

11. A Note on the Uniform Asymptotic Expansion of Integrals with Coalescing End Point and Saddle points
(C. Leubner)

Together with H. Ritsch of the University of Innsbruck we have introduced a new method for the uniform asymptotic expansion of certain types of contour integrals, one of whose critical points is an end-point of the interval of integration. The method, which is alternative to Bleistein's, has been tested numerically by way of a non-trivial physical example. The results will be published in Journal of Physics A: Mathematical and General.

12. Generalized Stirling Approximations to $N!$
(C. Leubner)

Generalized asymptotic approximations to $\Gamma(x+1)$, which contain an arbitrary parameter, are derived both from the integral representation of the Gamma function without assuming a knowledge of the Stirling series, and through elementary rearrangements of the Stirling series. By optimizing the arbitrary parameter according to appropriate criteria, several known Stirling-like approximations are recovered in a unifying way. These are as compact as but numerically superior to the standard Stirling approximations, and are meaningful on intervals that even include parts of the negative x -axis. It is pointed out that these results - arrived at by elementary but generally applicable asymptotic techniques - can be exploited in physics teaching to demonstrate the power and utility of asymptotic methods in the analysis of a variety of physics problems. The results are to appear in the European Journal of Physics.

13. Accurate Emission Spectra from Planar Strong Field Wigglers with Arbitrary Field Variation
(C. Leubner)

In collaborative work with H. Ritsch of the University of Innsbruck we showed that the spectral and angular distribution of the single particle wiggler signal can be conveniently evaluated by asymptotic complex contour integration, if the wiggler magnetic field is an arbitrary function of only the coordinate along the wiggler axis. The method is efficient and accurate, especially in the most interesting range of frequencies around the characteristic frequency of the wiggler, where for strong field wigglers the conventional procedure encounters serious

computational difficulties. The method exhibits promise for extensions in various directions of experimental interest. The results will appear in Nuclear Instruments and Methods in Physics Research.

14. Dynamical symmetries and equivalent Lagrangians for one-dimensional systems
(C. Leubner)

In collaboration with M. A. M. Marte of the University of Innsbruck we have shown that for one-dimensional Newtonian equations of motion a surjective mapping from the set of dynamical symmetries onto the set of equivalent first-order Lagrangians can be established, where - up to an integration - the Lagrangian associated with a particular dynamical symmetry is explicitly given.

15. On the Relationship of Normal Modes to Local Modes
(I. M. Mills)

A simple model for the effective vibrational Hamiltonian of the XH stretching vibrations in H_2O , NH_3 and CH_4 is considered, based on a Morse potential function for the bond stretches plus potential and kinetic energy coupling between pairs of bond oscillators. It is shown that this model can be set up as a matrix in local mode basis functions, or as a matrix in normal mode basis functions, leading to identical results. The energy levels obtained exhibit normal mode patterns at low vibrational excitation, and local mode patterns at high excitation. When the Hamiltonian is set up in the normal mode basis it is shown that Darling-Dennison resonances must be included, and simple relations are found to exist between the x_{rs} , g_{tt} , and K_{rrss} anharmonic constants (where the Darling-Dennison coefficients are denoted K) due to their contributions from Morse anharmonicity in the bond stretches. The importance of the Darling-Dennison resonances is stressed. The relationship of the two alternative representations of this local mode/normal mode model are investigated, and the potential uses and limitations of the model are discussed.

F. Future Plans

1. Calibration and Data Center Activities

During the coming year we will devote a major effort to the completion of "Microwave Spectral Tables III. Hydrocarbons". In conjunction with this manuscript we will produce a magnetic tape of the combined measured and calculated spectra which is too extensive to publish in printed form. Eventually we will combine this data with the existing files on diatomic and the triatomic species to form the initial spectral line atlas. We will also begin extracting and evaluating data on a new

group of organic species. Hydrocarbons containing the heteroatoms, oxygen or nitrogen will be selected for the next review in this series after we examine our files of literature references on these compounds.

In addition to the general search of the microwave literature we will continue searching the astronomy literature for interstellar molecular observations. Due to the rapid increase in new data during the 5 years between revision of the Recommended Rest Frequency publication, we plan to up-date the computer data files on a continuing basis in order to publish subsequent revisions in a shorter time frame. Publication of revisions every two years is the current plan.

Further work is planned in collaboration with NBS/Boulder on developing infrared calibration frequency standards. New heterodyne measurements on hot bands of N_2O will be performed to extend the present calibration tables into the 2800 cm^{-1} region. Preliminary results from this work have already been provided to workers at NBS in support of their work on NO_2 . Similar work will also be done on the $\nu_3+2\nu_2$ band of OCS near 1900 cm^{-1} as well as on the fundamental band of NO.

2. Spectroscopy for Environmental Studies

Work on the spectroscopy of molecules of importance in the chemistry of the earth's atmosphere will continue in support of NASA and CMA programs during the coming year. Intensity and frequency measurements will be made on ClO. New infrared diode laser measurements on the spectrum of nitric acid will be made and combined with existing microwave and infrared data to develop an atlas of transition frequencies and intensities for the range $1680-1740\text{ cm}^{-1}$. Work will also be done on the ν_5 and $2\nu_9$ bands of nitric acid. The analysis of these bands, which span the region from 850 to 930 cm^{-1} , requires the inclusion of a perturbation due to a $\Delta K=\pm 2$ interaction. Similarly, although the ν_3 and ν_4 bands of nitric acid have been assigned, they are found to be perturbed and are still to be satisfactorily analyzed.

The work on the collisional line-shapes of HF and HCl undertaken in support of the NASA project HALOE will be concluded during the coming year. We will examine the effects of collisions on the electronic fine structure of NO as well as for overlapping Q-branch transitions, and make precise frequency measurements on the fundamental band in collaboration with the NBS/Boulder group.

3. Spectroscopy of Hydrogen-Bonded and van der Waals Complexes

As first reported in the report for FY82 the High Resolution Group has embarked on a program of investigating the spectra of weakly bond molecular complexes and the present report indicates the expansion of these efforts. During the coming year we plan to continue to do tunable infrared laser spectroscopy of hydrogen bonded and van der Waals molecules. Using a coolable White cell with the gas under thermal equilibrium conditions investigations of hydrogen-halide complexes will be

continued with the difference frequency laser spectrometer while the diode laser spectrometer will be used in the study of heavier complexes (e.g. NO-dimer) as well as for the study of the far-infrared van der Waals modes of HX complexes.

Infrared investigations will also be performed on molecular-beam adiabatically-cooled systems. A pulsed molecular beam apparatus is now under construction and will be used for absorption spectroscopy with the aid of various tunable lasers. A cw-molecular-beam laser resonance apparatus is now under development and scheduled for completion during the coming year for vibrational predissociation measurements. Also under development is a high resolution tunable F-center laser system for high power excitation of van der Waals complexes for vibrational predissociation studies.

The good performance of the initial version of our pulsed-beam spherical Fabry-Perot cavity microwave spectrometer has prompted us to improve the sensitivity and efficiency of this instrument. Modifications of the hardware in the signal detection and digitization systems coupled with streamlined software will allow more rapid pulsing. Modifications are also planned to improve the search efficiency of the instrument by computer control of a number of current manually performed operations. With these modifications we expect a five-fold improvement in the spectral search over the present value of 100 MHz/day.

Several techniques are under investigation for producing pulsed beams of non-volatile materials e.g. thermo-spray and laser ablation methods, to broaden the range of studies possible with this spectrometer.

In addition to these instrumental improvements planned during the coming year we will engage in spectral studies of hydrogen-bonded species as well as van der Waals complexes. Several of these planned microwave investigations will be carried out in conjunction with the infrared studies done in the group.

The experimental studies planned for next year will be complemented by theoretical investigations. In particular work will continue on the problem of the water dimer.

4. General Spectroscopy

Several projects are planned in the realm of large amplitude motions such as the study of the torsional band of methyl alcohol and the spectrum of methyl amine. These projects will serve to further test the Hamiltonian models for rotation-vibration spectra for the case of large amplitude internal motions.

3. LASER PHOTOCHEMISTRY GROUP

D. F. R. Burgess, Jr., M. P. Casassa, R. R. Cavanagh, L. B. Elwell,
E. J. Heilweil, M. E. Jacox, D. S. King, D. A. Mantell, J. C. Mialocq,
J. Perry, J. C. Stephenson, and A. M. Woodward

A. Introduction

This group primarily does quantum-state specific studies of molecular dynamics. A common factor in the research described below is the role of energy transfer in the spectroscopy and kinetics of molecules. Research on molecular dynamics of molecules on surfaces is done in collaboration with the Surface Science Division.

The following staff changes have occurred in the year since July 1984. The 1984 annual report mentioned five post doctoral fellows working in this group. One of them (Woodward) remains at NBS as an NRC post-doc. Two (Perry, Mantell) left NBS to take permanent jobs in the private sector. Two (Heilweil and Casassa) agreed to join the Molecular Spectroscopy Division staff. Don Burgess (post-doc, Div. 541) came to NBS in January 1985 to study thermal and laser-induced desorption of molecules from surfaces. A visiting senior scientist, Dr. Jean-Claude Mialocq from CNRS (Saclay, France), spent eleven months on sabbatical at NBS where he did picosecond photochemistry and pulse radiolysis experiments.

B. Condensed Phase Energy Transfer

(M. P. Casassa, R. R. Cavanagh, L. B. Elwell, E. J. Heilweil,
J. Perry, J. C. Stephenson, A. M. Woodward)

The major effort in the condensed phase energy transfer program has been directed at the study of vibrational energy transfer (VET). During the past year we have successfully measured the rates of energy transfer from vibrationally excited chemical bonds in liquids, solids, and in molecules bound to surfaces.

For simplicity, the experimental results on VET have been organized in four sections: T_1 times for surface vibrations; T_1 for vibrations in liquids; T_1 for vibrations in solids; and T_2 times for vibrations in liquids. This distinction among studies of VET done in various phases of matter is not fundamental. At least for the non-metallic systems we have studied so far, VET is caused by short range forces, and the similarity of results for the same vibration in different phases is striking. This work is supported by AFOSR.

1. T_1 (Vibrational Energy Relaxation) times for vibrations on surfaces

We used an infrared pump/probe method to do time-resolved measurements of the vibrational energy relaxation rate (T_1^{-1}) for the high frequency modes of species chemisorbed on a silica (SiO_2) surface in a variety of chemical environments. Previously, energy transfer rates have been measured for the vibrations of many molecules in the gas phase, and for a few molecules in liquids and low temperature solids. However, our experiments were the first to measure vibrational energy transfer rates for vibrations on surfaces.

Our initial measurements were on the surface hydroxyls (OH) bound to dispersions of colloidal fumed silica (Degussa Aerosil 200, 120 Å diameter particles, 200 m^2/gm surface area). We have since measured T_1 for several different surface vibrations at the solid-vacuum interface and at the solid-liquid interface. We explain the method for the OH-stretch ($\nu=3750 \text{ cm}^{-1}$) vibration; the same technique was used for all the vibrations we have studied. The surface hydroxyl $\nu=0 \rightarrow 1$ transition at the SiO_2 -vacuum interface was excited with a strong picosecond IR pulse which transferred up to 10 percent of the hydroxyls from the $\nu=0$ to $\nu=1$ level. Due to anharmonicity, OH ($\nu=1$) does not absorb at the pump frequency, so excitation causes a transient increase in sample transmission, T . As population relaxes, the sample transmission returns to its equilibrium value, T_0 ; $\ln(T/T_0)$ is proportional to OH ($\nu=1$) population. Recovery of sample transmission was monitored by a weak, time-delayed probe pulse derived from the saturating pulse and a variable optical delay. At each time delay (t_D), the probe pulse transmission was measured to 0.3 percent accuracy with pump excitation and with the pump blocked using a dual pyroelectric detector energy ratiometer. A typical data run is shown in Figure 3.1. The population in OH ($\nu=1$) decreases exponentially with a characteristic decay time of $T_1 = 216 \text{ ps}$.

The picosecond apparatus used in this investigation was based on a modelocked Nd^{+3} :YAG laser. Single 1.06 μm pulses of ~35 mJ and 10 Hz repetition rate pumped a chain of three LiNbO_3 crystals (OPA) to parametrically generate tunable infrared picosecond radiation, which had a spectral bandwidth of 15 cm^{-1} FWHM, duration of 20 ps FWHM, and delivered about 400 μJ of pump energy to the sample.

The room temperature results for several surface vibrations, at the solid-vacuum and solid-liquid interface are given in Table 3.1. For all these systems, the bulk substrate SiO_2 was the same (fundamental substrate modes are less than 1200 cm^{-1}). The T_1 lifetime for OH($\nu=1$) on SiO_2 in vacuum corresponds to roughly 2×10^4 vibrational periods. In various solvents the OH($\nu=1$) T_1 lifetime decreases as the highest solvent fundamental vibrational mode frequencies approach the 3700 cm^{-1} OH frequency. This is particularly evident for CH-stretch (~3000 cm^{-1}) containing molecules such as CH_2Cl_2 and C_6H_6 where $T_1 = 102 \pm 20 \text{ ps}$ and $87 \pm 30 \text{ ps}$, respectively.

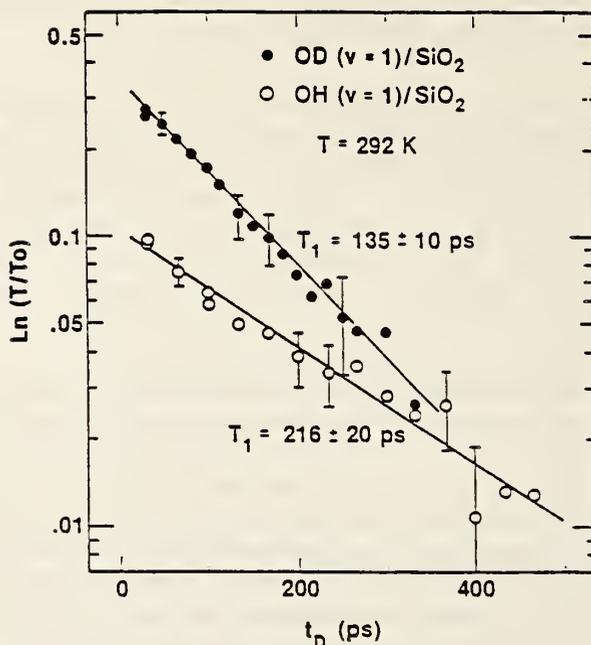


Fig. 3.1. T_1 decay for isolated surface OD($v=1$) and OH($v=1$) on a dried evacuated SiO₂ disk at $T=293$ K. The exponential recovery of transmission as a function of probe delay (t_D) yields a lifetime of $T_1 = 135 \pm 10$ ps for OD($v=1$) and $T_1 = 216 \pm 20$ ps (1σ) for OH($v=1$) from a least squares fit.

In the presence of adsorbed H₂O, which possesses a broad, partially overlapping OH absorption with SiOH, T_1 reduces even further to ~ 56 ps. In this case, direct V-V transfer from the surface OH to adsorbed water may participate in the deactivation process.

Insight into vibrational energy transfer at surfaces may be gained by studying other species bound to the silica substrate. In this way the potential accepting modes of the bulk material remain unchanged while the adsorbate local modes and adsorbate-substrate coupling are modified. The simplest substitution for the OH group is isotopic exchange to OD. In this case T_1 is reduced from 220 ps for SiOH to 150 ps for SiOD (as pressed disks in vacuum). Decay of the lower energy OD quantum into the substrate was expected to require fewer lattice quantum transitions than for OH (i.e., $\Delta v \geq 3$ vs. $\Delta v \geq 4$) and result in faster decay rate. However, the observed isotope effect was smaller than anticipated.

The hydroxyl T_1 lifetime for BOH modified silica ($\nu_{OH} \sim 3700$ cm⁻¹) in vacuum or CCl₄ is found to be ~ 70 ps. Since the boron mass and coordination to the surface oxygens is different from silicon, changes in the local site bending and stretching frequencies must occur. This surface modification is found to substantially alter the relaxation lifetime of the surface OH species. Both NH-stretching modes of -NH₂ were found to saturate to the same extent ($\Delta T/T \sim 5\%$) although time-resolved measurements produced an instrumental pulsewidth-limited response. While precise T_1 values could not be deduced from these results, the two modes

apparently exchange population rapidly and have comparable lifetimes (≤ 20 ps). Attempts to saturate the CH-stretching transitions of $-\text{OCH}_3$ were unsuccessful, however. This may imply very fast vibrational relaxation ($T_1 < 5$ ps) for the CH-stretches of chemisorbed methoxy. The above results for adsorbates on SiO_2 suggest that increasing the complexity of adsorbate vibrational level structure leads to more rapid vibrational energy relaxation at the silica surface.

We have not yet directly measured where the energy goes when it leaves the initially excited high frequency vibrations. To obtain indirect evidence concerning the effective lattice accepting modes, we studied the isotope and temperature dependence of $\text{OH}(v=1)$ relaxation at the SiO_2 -vacuum interface. The results are shown in Figure 3.2. The solid lines show fits to the data using the theory of multiphonon relaxation in solids. For OH, the observed T dependence is well fit by a $n=4$ quantum process, i.e. $\nu_{\text{OH}}(3750) \rightarrow 4\nu_{\text{lattice}}$. For OD the data are best fit by $n=3$, i.e. $\nu_{\text{OD}}(2760) \rightarrow 3\nu_{\text{lattice}}$.

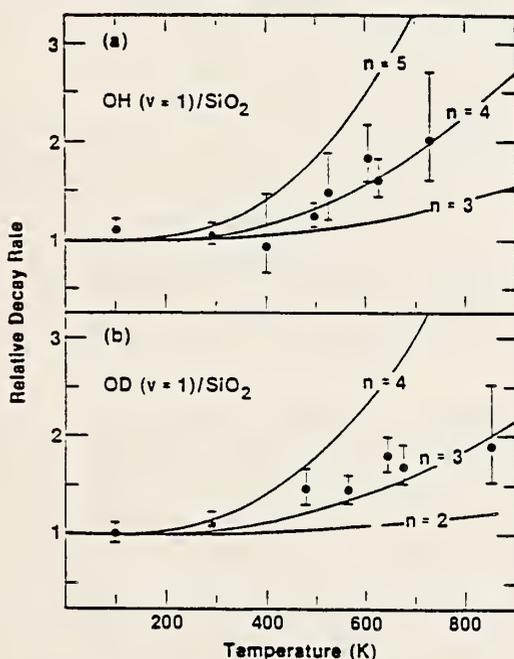


Fig. 3.2 Decay rates, T_1^{-1} , for $\text{OH}(v=1)$ and $\text{OD}(v=1)$ on a dried evacuated SiO_2 disk as a function of temperature T . Rates have been normalized by dividing the OD rates by $1/149$ ps = 6.7×10^9 s $^{-1}$, and the OH rates by $1/220$ ps = 4.5×10^9 s $^{-1}$. Error bars give the 1σ uncertainty in rate. The solid curves give the relative multiphonon relaxation rates vs. T for an n -phonon process (see text).

Table 3.1. T_1 vibrational decay times at room temperature for the various adsorbate/silica systems studied.

System	$\nu(\text{cm}^{-1})$	$T_1(\text{ps})$	$k(10^9 \text{ s}^{-1})$	$k'(10^9 \text{ s}^{-1})^a$	Notes
SiOH/vacuum	$\nu_{\text{OH}}=3750$	220 ± 20	4.9	-	Pressed SiO_2 disk
SiOH/ CCl_4	$\nu_{\text{OH}}=3690$	159 ± 16	6.3	1.4	Dry SiO_2 dispersion
SiOH/ CF_2Br_2	$\nu_{\text{OH}}=3690$	140 ± 30	7.1	2.2	"
SiOH/ CH_2Cl_2	$\nu_{\text{OH}}=3660$	102 ± 20	9.8	4.9	"
SiOH/ C_6H_6	$\nu_{\text{OH}}=3625$	87 ± 30	11.0	6.1	"
SiOH/ C_6D_6	$\nu_{\text{OH}}=3625$	80 ± 30	12.0	7.1	"
SiOH/ $\text{H}_2\text{O}/\text{CCl}_4$	$\nu_{\text{OH}}=3690$	56 ± 10	18.0	13.0	SiOH T_1 , -5 $\text{H}_2\text{O}/100\text{A}^2$ physisorbed
SiOD/vacuum	$\nu_{\text{OD}}=2760$	155 ± 16	6.5	-	OD T_1 with 67% OH re- placed by OD
BOH/vacuum BOH/ CCl_4	$\nu_{\text{OH}}=3700$	~ 70	~ 14.3	-	Early decay time; long time com- ponent present
SiNH ₂ /vacuum SiNH ₂ / CCl_4	$\nu_{\text{NH}}=3460$ 3520	< 20 -	> 50	-	Pulsewidth limited signal, $\Delta T/T$ -5% for both stretches
SiOCH ₃ /vacuum	$\nu=2860$ 3000	$< 5(?)$	$> 280(?)$	-	No pulse saturation observed for any CH- stretching mode

^a $k' = k - k_{\text{vacuum}}$

Acceptor mode frequencies compatible with this simple theory are also consistent with the known frequencies of modes spatially near and hence likely to be coupled to the surface OH($v=1$). For example, the Si-OH stretch occurs at 970 cm^{-1} , the Si-O-H bend at 795 cm^{-1} , and Si-O stretching vibrations produce broad maxima at 800 and 1100 cm^{-1} in the vitreous silica phonon spectrum. The temperature dependence of the multiphonon theory is inconsistent with energy going to the surface Si-OH torsion vibration at 380 cm^{-1} (or to SiOD at $\omega_i \approx 270\text{ cm}^{-1}$). The $n=4$ process for OH($v=1$) and the $n=3$ process for OD($v=1$) are in fact the lowest order processes possible, in keeping with the propensity rule that the most probable relaxation path will require the fewest simultaneous changes of vibrational quantum numbers.

The observation that OD on the surface relaxes faster than OH is qualitatively consistent with the expected increase of T_1 with increasing energy gap between the excited level and the frequency of the accepting modes. Multiphonon theories give the low T rate, $\gamma(0)$, as $\gamma(0) = a\exp(-b\omega)$ or $\gamma(0) = a(\epsilon)^n$ where ω is the OH or OD frequency, n the order of the process, and the constants a , b , and ϵ ($\epsilon < 1$) depend on molecular structure. However, it is surprising that the increase is only a factor of 1.5 (220 ps OH vs. 150 ps OD; $\epsilon = .68$) when the energy difference is 1000 cm^{-1} . For comparison, measurements of the spin-orbit relaxation of ions in crystals give values of ϵ in the range 0.037 to 0.2 (i.e., the rate for an n phonon decay is 5 to 27 times faster than an $n + 1$ phonon decay in the same solid). We used a simple multiphonon relaxation theory to estimate the relative rates for a 3 phonon (OD) and 4 phonon (OH) relaxation of SiO_2 . If the accepting modes ($\omega_i \approx 930\text{ cm}^{-1}$) are the same, theory predicts $\gamma(0)$ for OD should be 13 times $\gamma(0)$ for OH ($\epsilon = .077$). Although theoretical estimates of the anharmonic coupling strength, and hence of ϵ , are uncertain, it seems difficult to reconcile the multiphonon theory to both the isotope and temperature dependence.

In addition to the multiphonon theory, we have considered other mechanisms of VET for these surface vibrations. The damping of vibrational energy is not due to coupling to an image dipole formed in the substrate, nor is damping by electron hole pair formation possible for vibrations on a dielectric like SiO_2 . Förster energy transfer (site hopping) is not important because of the small transition dipole moments ($\mu_{\text{OH}} = .035\text{ D}$) and sparse adsorbate density (\leq four OH/ 100 \AA^2 surface). For molecules like CCl_4 and CF_2Br_2 , which have only low frequency vibrations, VET to the solvents is unimportant, although the internal high frequency modes of solvents like C_6H_6 may accept some of the energy.

Any theoretical approach to VET for vibrators on these dielectric surfaces must also take account of the data available for VET in solids and in liquids. Perhaps molecular dynamics simulations and classical trajectory studies will provide a consistent method of understanding the observed T_1 values. Certainly a direct measurement of the pathways (i.e. accepting modes) of VET will be of crucial importance to further the understanding of this subject (c.f. Future Plans).

Spectral linewidths observed in surface vibrational spectroscopy have sometimes been interpreted as T_1 uncertainty broadening. However, the width of the absorption features on silica surfaces must arise from site inhomogeneities or other dephasing processes, since the linewidths corresponding to T_1 are 200 to 2000 smaller than observed. Note that similar remarks pertain to T_1 vs spectral linewidths for the solids and liquids described in the next two sections.

2. T_1 times for vibrations in liquids

Although there have been thousands of measurements of VET rate constants for gas phase molecules where relaxation is caused by bimolecular collisions, there is very little information available (≤ 20 measurements) about T_1 times in room temperature liquids.

Over the past nine years, picosecond laser techniques have been used by several research groups (most notably Laubereau, Kaiser, et al., and Chesnoy and Ricard) to measure vibrational energy relaxation times for particular vibrational modes in room temperature liquids. Chesnoy and Ricard measured T_1 for neat liquids of the simple diatomics HCl, DCl, HBr, and DBr. They found that the liquid phase relaxation rate constants were comparable to gas phase rate constants when corrections for dimer formation in the liquids were taken into account.

Kaiser and Laubereau (KL) measured T_1 for the stretching vibrations ($\nu_{\text{CH}} \approx 3000 \text{ cm}^{-1}$) of eleven different hydrocarbons in solution (mostly dilute in CCl_4). They found T_1 varying from $< 2 \text{ ps}$ (C_2H_2 , CCl_3H) to 100 ps (CH_3CCl_3). The dependence of T_1 on molecular complexity was surprising (i.e. why should a simple molecule with only one high frequency mode like CCl_3H relax rapidly while complicated molecules like acetone or trichloroethane relax 50 times slower?).

We have recently measured T_1 for the OH and OD stretching vibrations of several alcohol and silanol molecules in dilute room temperature CCl_4 solution using the same experimental technique as for the surface studies. In part these experiments were done for comparison to the results of KL. Of particular significance to our program is the comparison between T_1 for vibrations such as OH, OD, and NH_2 bound to the surface of a dielectric such as SiO_2 , and T_1 for these same functional groups attached to a small molecule (dissolved in a liquid like CCl_4 which has vibrational frequencies comparable to those of SiO_2). If coupling to nearest neighbor vibrational motions determines the VET rates, then those small molecules may exhibit similar lifetimes to the surface systems.

The results we have obtained to date are shown in Table 3.2. T_1 times for the OH ($\sim 3690 \text{ cm}^{-1}$) and OD ($\sim 2720 \text{ cm}^{-1}$) stretching vibrations bound to the Si atoms of silanols (in CCl_4) are long. The T_1 values are similar to those for OH and OD bound to the Si atoms on a silica surface either at

Table 3.2. Vibrational relaxation times for OH(v=1) and OD(v=1) bonds of alcohols and silanols dilute in CCl₄ at T = 295K.

Alcohols	T ₁ (ps)		Silanols	T ₁ (ps)
Me ₃ COH	<15	←→	Me ₃ SiOH	205
Me ₃ COD	<15	←→	Me ₃ SiOD	245
Et ₃ COH	<15	←→	Et ₃ SiOH	185
Et ₃ COD	<20	←→	Et ₃ SiOD	224
φOD	<15		φ ₃ SiOH	206
C ₆ F ₅ OD	<15		φ ₃ SiOD	292
CH ₃ OH	<30		φ ₂ Si(OH) ₂	85
CD ₃ OH	73			
CH ₃ OD	52		φ ₂ Si(OD) ₂	134
CD ₃ OD	79			
C ₂ H ₅ OH	70			
Accuracy ±20%				

the vacuum interface or interacting with liquid CCl₄. For the surface species in vacuum, OD relaxes 50% faster than OH; for the liquid silanols the OH relaxation rate is systematically slightly faster than the OD rate.

The relaxation rates for OH (~3620 cm⁻¹) and OD (~2680 cm⁻¹) stretches in alcohols are much faster than for the corresponding silanols. For most alcohols T₁ was too fast for us to measure accurately (T₁ ≤ 15 ps); only for deuterated methanols and ethanol (OH) was T₁ long enough to be determined. For the four instances where we studied both silanols and the corresponding carbinols (i.e. Si substituted for central C), T₁ is at least twelve times shorter for the OH or OD groups when bound to C than when bound to Si. We are presently trying to interpret these results in terms of coupling to specific adjacent vibrational modes and determine if these rates relate to the chemical properties of these molecules.

All the T₁ results to date have been obtained with the one color IR pump/probe method. With the aid of a new low f-number Raman spectrometer (acquired in August, 1985), we hope to do further experiments on VET in liquids, using the technique of IR vibrational excitation followed by

spontaneous anti-Stokes Raman scattering (SPARS) probing (with harmonics of the Nd-YAG) of population in particular vibrational levels of these and other systems. For example, if we probe the OH, NH, or OD vibrations initially populated by the IR pulse, then we should obtain the same T_1 values deduced from the IR probe experiments. This will be an independent verification of these results. Of more importance, the SPARS experiments should permit us to identify the pathways of energy transfer (i.e., what are the lower frequency accepting modes) during the relaxation. For instance, using the IR pump/SPARS probe method, KL found that T_1 for the CH-stretch in ethanol is 40 ps, and we found T_1 for the OH stretch is 70 ps. If the CH stretching modes are transiently populated following excitation and relaxation of the higher frequency OH-stretch, we should be able to identify the rise and fall times of population in those modes. Of course, by tuning our OPA to pump CH stretches, we could also independently do the KL experiments.

3. T_1 for vibrations in solids

The IR pump/probe technique described above was also used to determine T_1 times for hydroxyl stretching vibrations in both amorphous and crystalline solids. T_1 times for hydroxyl groups coordinated to atoms (ions) in a variety of crystals have been studied in order to assess the importance of different local environments, including the mass of the metal atoms (heavy atom effect) on VET. It may be easier to model, e.g. via molecular dynamics simulations, the relaxation of bonds in these crystalline materials than for liquids or amorphous solids like fused silica.

The temperature dependence ($T \leq 1450\text{K}$) of the relaxation rate (T_1^{-1}) of OH ($\nu=1$) impurity oscillators inside fused silica is given in Figure 3.3. Note that the intrinsic vibrational relaxation rate for the bulk OH at room temperature is twice as fast as that for the surface OH on SiO_2 . The T-dependence is perfectly fit by the multiphonon relaxation theory for an $n = 4$ process, i.e. $\nu_{\text{OH}} (3690) \rightarrow 4\nu_{\text{lattice}}$. The OH impurity concentration in fused silica is so small (≤ 460 ppm) that no dependence of T_1 on OH concentration was observed.

The room temperature relaxation times for OH($\nu=1$) ions inside samples of crystalline mica have very recently been measured. In these crystals, OH is part of the unit cell, and the interatomic distances, the vibrational frequencies and the orientation of the OH bonds with respect to the crystallographic axes are known. In the mineral muscovite, formula $[\text{O}_{10}\text{Al}_3\text{Si}_3(\text{OH})_2\text{K}]_2$, the OH groups have a frequency of 3630 cm^{-1} . There are four equivalent hydroxyls per unit cell, located in a plane such that each is hexagonally surrounded by O atoms, and each OH is coordinated to two Al ions. For these OH groups, $T_1 = 100 \pm 20\text{ps}$. In the mineral biotite, Mg ions are substituted for some of the Al ions in muscovite, and two

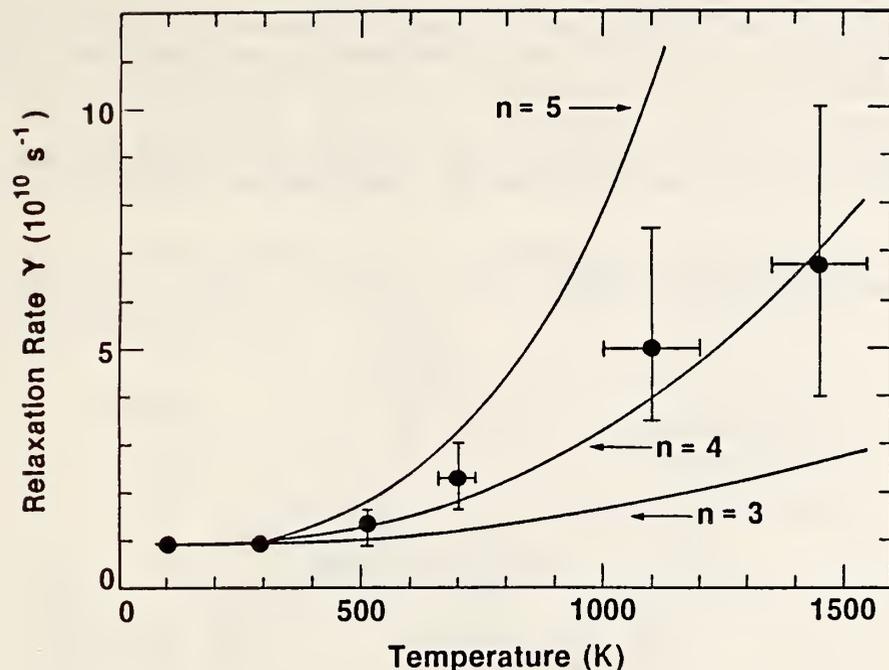


Fig. 3.3. Temperature dependence of the vibrational relaxation rate, $1/T_1$, of OH ($\nu=1$) impurity oscillators in bulk fused silica. The solid curves give the relative multiphonon relaxation rates vs. T for an n -phonon process (see text).

different OH species ($\nu=3660, 3590 \text{ cm}^{-1}$) occur. For the 3660 cm^{-1} vibration, $T_1 = 210 \pm 20 \text{ ps}$. These results are too recent to permit a detailed interpretation at this time. It should be emphasized that the high frequency lattice vibrations in these crystals are similar to those of fused SiO_2 , and the measured T_1 values are similar to the values found for the surface OH on SiO_2 , for the bulk OH in SiO_2 , and for OH bound to Si atoms of silanol molecules in liquid CCl_4 .

4. T_2 (Vibrational dephasing) times for vibrations in liquids

Picosecond coherent anti-Stokes Raman scattering (CARS) determined the dephasing times (T_2) for vibrations in simple liquids. Dephasing rates ($2/T_2$) were determined at $T=295\text{K}$ for the symmetric stretch of CS_2 ($\nu_1=656 \text{ cm}^{-1}$) as a function of mole fraction in several solvents, and as a function of temperature in neat CS_2 . Also, the dephasing rate of the ring breathing mode of benzene ($\nu = 991 \text{ cm}^{-1}$) was studied as a function of its dilution in CS_2 .

Since neither the apparatus nor the results have previously been described in an Annual Report, details of both will be given below. We do not anticipate any further studies of dephasing rates. However, the apparatus used for the T_2 measurements, with some modification, will be

used in several future experiments, e.g. measurements of T_1 for $\text{CO}(v=1)$ on Pt(111) and measurements of vibrational predissociation times for van der Waals molecules.

The apparatus is shown in Figure 3.4. Two dye lasers of independently tunable wavelength (via 3 plate intracavity birefringent filters)

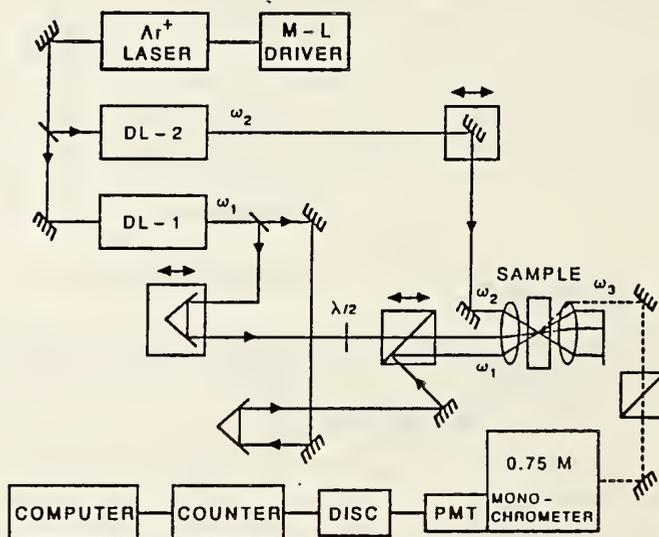


Fig. 3.4. Schematic diagram of apparatus used to measure T_2 for vibrations in simple liquids by picosecond CARS.

are synchronously pumped by a modelocked Ar^+ laser operating at 82 MHz. Tunable dye laser pulses at that repetition rate had about 0.6 nJ energy, an autocorrelation width (FWHM) of 8 ps, and a spectral bandwidth (FWHM) of 2.5 cm^{-1} . If the pulses were Gaussian, this would correspond to a $\Delta\nu\Delta t$ product of 0.42, very close to the transform limit. The width of the cross correlation was about the same as the autocorrelation. A cw modelocked Nd-Yag laser (scheduled for delivery in November 1985) will replace the Ar^+ laser in future experiments. Uncompressed dye laser pulses of 0.5 ps duration have been reported with (doubled) Nd-Yag pumping.

In our CARS experiment, the frequency difference between the dye lasers ($\omega = \omega_1 - \omega_2$) was chosen to be resonant with the vibrational mode to be studied. Pulses at ω_1 and ω_2 , vertically polarized and overlapped in time were incident on the sample at the phase-matching angle. The pair of pump pulses creates a coherent vibrational excitation in the liquid at frequency $\omega_1 - \omega_2$. At a delayed time t_D a probe pulse at frequency ω_1 , horizontally polarized, is sent through the sample in the correct propagation direction for phase matching the anti-Stokes frequency $\omega_3 = 2\omega_1 - \omega_2$. A CARS signal (different in both frequency and propagation direction from the other beams) is generated by this pump pulse. The intensity (i.e. pulse energy) of the CARS signal decays in time after the

pump pulses as $S(t_D) = \exp(-2t_D/T_2)$. The CARS signal, spatially and spectrally filtered to eliminate scattered dye laser light, is detected by a cooled photomultiplier operated in the pulse counting mode, and the count rate is constantly stored in a computer. When necessary, neutral density filters are inserted in the CARS beam to keep the count rate much less than 82 MHz.

A typical experimental run to determine T_2 for the symmetric stretch of liquid CS_2 is shown in Figure 3.5. Counts were summed for 10 sec at each delay stage position t_D .

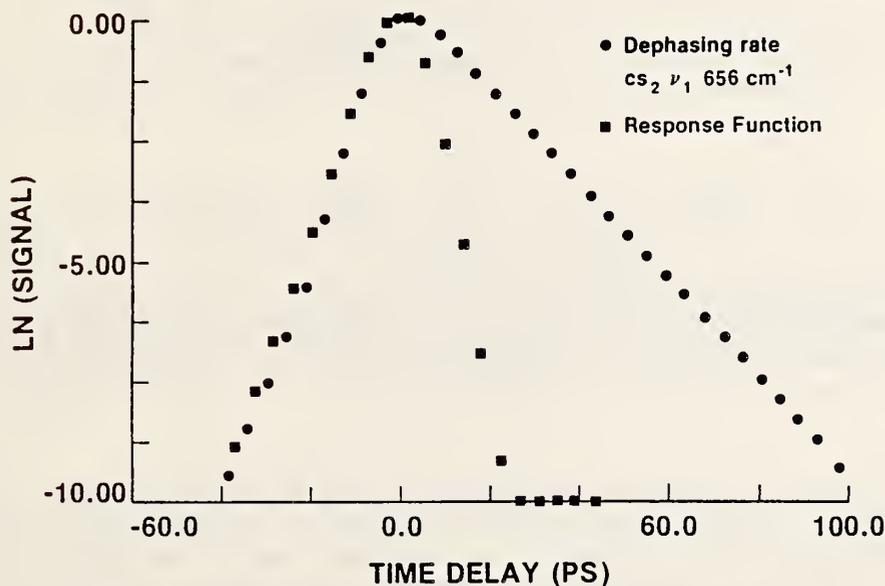


Fig. 3.5. Typical experimental run for the determination of the vibrational dephasing time T_2 for the totally symmetric stretching vibration $\nu_1 = 656 \text{ cm}^{-1}$ of CS_2 in the liquid state.

The CARS signal decays exponentially over at least 10 e-folding times, with a characteristic decay time $T_2/2 = 10.2 \pm 0.2 \text{ ps}$. This result for neat CS_2 agrees with previous work. Also shown in Figure 3.5 is the measured apparatus response function for this experiment. For $t_D > 10 \text{ ps}$, the third order response function has a characteristic exponential decay time (1/e point) of 1.8 ps. Therefore, if the CARS signal is sufficiently strong, one may determine values of $T_2/2$ almost as short as this response time, despite the fact that the cross correlation FWHM is 8-9 ps. The shortest T_2 we report below is 5.2 ps.

A summary of the room temperature dephasing rates of CS₂(100) in various liquid mixtures is shown in Figure 3.6. When CS₂ is diluted in

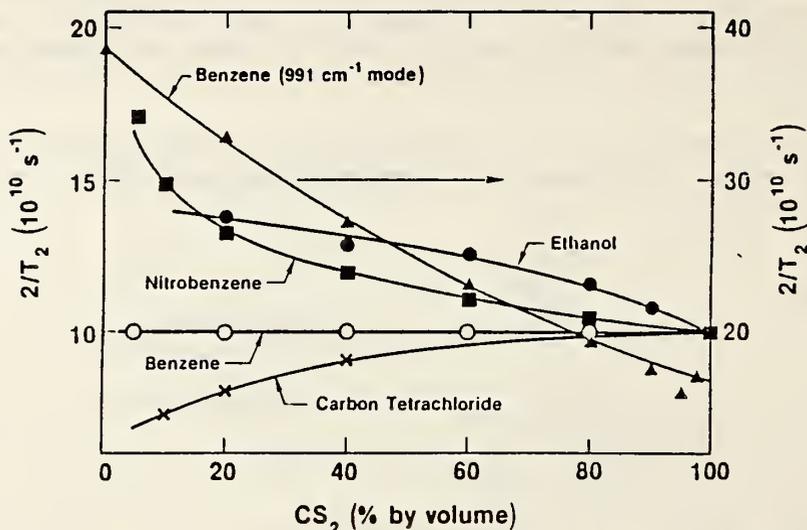


Fig. 3.6. Room temperature dephasing rates ($2/T_2$) of CS₂ in the totally symmetric vibrational state $\nu_1 = 656 \text{ cm}^{-1}$ in various liquid mixtures. The points designated by filled triangles (Δ) are for the ring breathing mode of benzene ($\nu = 991 \text{ cm}^{-1}$) in CS₂.

CCl₄, the dephasing rate decreases compared to the pure CS₂ rate. On dilution in benzene, T_2 for CS₂ (100) is constant. Nitrobenzene, which has a large permanent dipole moment, and ethanol, which can form hydrogen bonds to other liquids, significantly decrease the dephasing rate of CS₂ (100). This is probably due to the stronger long range forces that these molecules can exert on CS₂.

Also shown in Figure 3.6 is the dephasing rate of the ring breathing mode of benzene ($\nu=991 \text{ cm}^{-1}$) in CS₂. Our result for pure benzene ($T_2 = 5.2 \text{ ps}$) agrees with previous measurements. As benzene becomes more dilute in CS₂, $2/T_2$ decreases. At low concentrations, so that each benzene molecule is surrounded by CS₂, T_2 increases by a factor of 2.5 ($T_2 = 12 \text{ ps}$). This is completely different behavior from the relaxation of CS₂(100) for which T_2 was independent of CS₂/benzene ratio.

We are presently working on the interpretation of these data. Although the data in Figure 3.6 do not give straight lines, it nevertheless appears that all the rates are consistent with an isolated binary collision (IBC) expression of the form

$$2/T_2 = \rho \times k_{ii} g_{ii}(\sigma) + \rho (1-x) k_{ij} g_{ij}(\sigma)$$

where x is the mole fraction of the molecule for which T_2 was determined, ρ the liquid density, $g_{ij}(\sigma)$ the radial distribution function at separation σ , and k the bimolecular dephasing rate constants ($\text{cm}^3/\text{molecules}/\text{sec}$).

We have also measured the dephasing rate of neat CS_2 as a function of temperature from its freezing point at $T=165\text{K}$ to $T=298\text{K}$. Over the range $210\text{K} < T < 300\text{K}$ the rate decreases; then as T decreases further, $2/T_2$ increases from $8.2 \times 10^{10} \text{s}^{-1}$ at 210K to $11.2 \times 10^{10} \text{s}^{-1}$ at $T = 170\text{K}$. These time-domain data may be compared to earlier frequency domain results for the isotropic Raman linewidth $\Delta\nu$ of $\text{CS}_2(100)$. In principle, $2/T_2 = \Delta\nu$ (FWHM). The agreement is only fair. In this case the picosecond measurements are probably more accurate, since the linewidths are narrow (hence difficult to resolve), and since the slope of the line in Figure 3.5 can probably be determined with more accuracy than a Lorentzian can be fit to the Raman spectral line. We are presently interpreting these temperature-dependent results.

These T_2 experiments have supported the T_1 measurements which have been done or are planned. Both T_1 and T_2 experiments in liquids (or at the solid/liquid interface) can make use of similar theoretical treatments (which we are now attempting). The T_2 experiments have played a crucial role in developing and testing our ability to use the synch-pumped lasers which (when amplified) will form the basis for many future T_1 measurements.

C. Desorption of Molecules from Surfaces

(D. F. R. Burgess, Jr., R. R. Cavanagh, L. B. Elwell, D. S. King and D. A. Mantell)

A dedicated experimental facility including surface sensitive analysis (e.g., mass spectrometer, argon ion sputtering, LEED and Auger electron spectrometer), computer controlled data acquisition and sub-Doppler (250 MHz) laser resolution is being applied to the study of the thermal desorption of molecules chemisorbed on well characterized surfaces. Results in past years have emphasized the $\text{NO}/\text{Ru}(001)$ system.

In FY'85 measurements of the internal state distributions for NO desorbing from a saturation coverage of NO on $\text{Pt}(111)$ were published as a communication in *J. Chem. Phys.* Results for an extensive study of the NO coverage dependence, over a ten-fold range in coverage, and the influence of co-adsorbates has been submitted to *J. Chem. Phys.* The results of the work on the $\text{NO}/\text{Pt}(111)$ system may be summarized as follows: 1) the rotational levels and spin-orbit states are characterized by a common rotational temperature; 2) although the kinetic parameters describing the desorption process change significantly with coverage and the presence of co-adsorbed CO , the rotational degree of freedom of the desorbing NO is always nearly fully accommodated with the surface temperature; 3) there was no measurable alignment of the desorbing species.

The results of a series of thermal desorption experiments following saturation coverage of NO on Pt(111) are shown in Figure 3.7. The solid

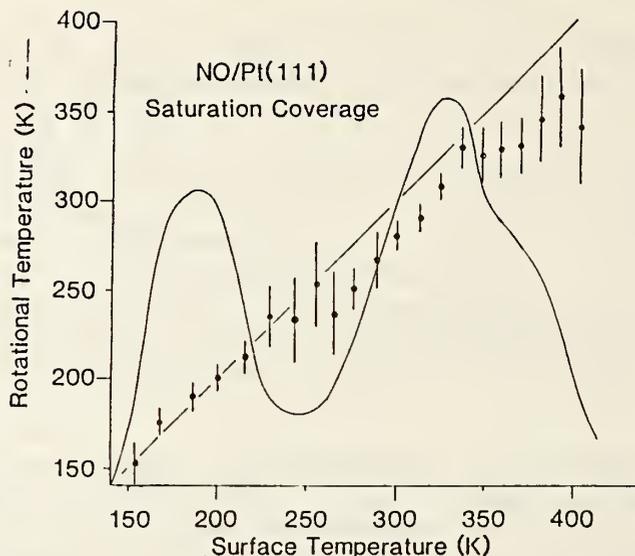


Fig. 3.7. Dependence of rotational temperature of NO desorbed from a saturation covered Pt(111) surface at various substrate temperatures.

curve is a thermal desorption spectrum obtained using a mass spectrometer to measure the total NO desorption as a function of increasing surface temperature. The data points (with 2 sigma error limits) give the measured rotational temperatures describing the NO species desorbed during intervals of 20 K (during a period of 2 sec) during the desorption heating ramp. There are two distinct desorption features for the NO/Pt(111) system and from this figure it becomes obvious that the rotational temperature of the desorbing species follows the instantaneous surface temperature for both features. All this data fits in the narrow range of having the rotational temperature being equal to $95 \pm 5\%$ of the surface temperature.

Despite the fact that these results are consistent with the expectations from transition state theory, such a theory would lead to the additional expectation of a desorbing angular flux described by the cosine law and a Maxwellian kinetic energy distribution at the surface temperature. Preliminary results on Doppler profile measurements for NO desorbing from saturation coverages from Pt(111) indicate that these expectations are not upheld. These measurements show equivalent Doppler profiles for NO species desorbing in all final rotational states in the range of $2.5 < J < 15.5$, with energies from $13 < E_p < 426 \text{ cm}^{-1}$, indicating no dependence of final kinetic energy on rotational state. Both the

rotational state distributions and the dependence of kinetic energy on final rotational state are markedly different for the reactive NO/Ru(001) versus the non-reactive NO/Pt(111) systems.

Thermal desorption samples processes occurring under "equilibrium" conditions; this is to say that a heating rate of 10K/sec is much slower than molecular energy transfer processes in condensed phases. We have initiated a study of direct desorption processes following rapid heating of the surface using non-resonant laser irradiation. Here it is hoped that the short time scales for heating, i.e., 1-10 nsec. might allow desorption to compete favorably with other energy exchange or relaxation processes. Progress to date includes the assembly of an ultra-high vacuum chamber designed for laser-heating/final-state resolved measurements. Initial measurements have focussed on obtaining reproducible laser desorption signals and achieving an understanding of the dependence of desorption probability versus laser pulse energy. This work is supported by DOE.

D. Dynamics of van der Waals Molecules

(M. P. Casassa, L. B. Elwell, D. S. King, J. C. Stephenson and A. M. Woodward)

These experiments represent a new direction of research, in part an outgrowth of infrared multiphoton photodissociation experiments. The experiments consist of the characterization of the time scales and final state distributions in the dissociation of van der Waals complexes excited to well-defined vibrational or electronic states. The systems studied during FY '85 included the electronic predissociation of NO-Ar, and the vibrational predissociation of both NO-ethylene and NO-NO. The van der Waals species were formed in a pulsed free jet expansion. Mass spectrometric techniques have been used to characterize the cluster distributions formed in our beam as a function of backing gas composition and pressure. The dynamics studies consisted of a one-photon laser excitation to a predissociating state, followed by measurements of the rotational (J), spin-orbit (Ω), and lambda doublet (Λ^+/Λ^-) distributions of the NO photoproducts via laser excited fluorescence of the A--X transition at 226 nm. The spatial distribution of J-vectors (alignment) and the velocity distribution (both speed and angular flux) were determined by polarization and Doppler techniques.

NO-Ar undergoes an electronic excitation to the NO-like $3s\sigma$ A state at excitation frequencies near $44,200\text{ cm}^{-1}$. Although excited Π states of the NO-Ar species are stable and exhibit discrete electronic absorption spectra, the $A^2\Sigma$ state is distinctly different. This is a Rydberg state, with an electronic orbital radius that extends well beyond the NO-Ar separation in the electronic ground state. Thus, in the Franck-Condon excitation process, the excited state created through the absorption process is more analogous to $\text{NO}^+\text{-Ar}$, which should be more tightly bound and have a shorter van der Waals radius. The result of this is that there is a predissociative curve crossing involving the ground state potential energy surface. The NO fragments formed in this predissociation are predominantly in the electronic ground state (>99%) and exhibit Doppler

profiles that indicate that the lifetime of the electronically excited parent is substantially less than a rotational period -- i.e., on the order of or less than a few periods of the van der Waals vibration. Very little of the total available energy appears as rotational excitation of the fragments -- only about 0.5%. Presumably this reflects a constraint imposed in the conservation of angular momentum.

There has been substantial recent theoretical interest in the vibrational predissociation of van der Waals molecules, but very few experiments that have looked at either the final state distributions or obtained real time measurement of the dissociation lifetimes. Earlier measurements (by Hoffbauer, Liu, Giese and Gentry and by Bomse, Cross and Valentini) of the kinetic energy released in the dissociation of the ethylene dimer excited at 950 cm^{-1} to the ethylene ν_7 mode indicated, in consonance with theoretical expectations, that most of the available excess energy went into rotational excitation of the two ethylene fragments. In our experiments on NO-ethylene excited to the same ethylene-like ν_7 mode by our short pulse CO_2 laser we found very little rotational excitation in the NO fragment and very little kinetic energy released. Equal populations were found in the two NO lambda doublets. This contrasts with the disequilibrium of lambda states found in the products of the prompt electronic photodissociations of HOH and HONO and in many direct collisional H-atom abstraction reactions. Presumably, most of the available excess energy (i.e., roughly 50%) went into excitation of a-axis rotation in the ethylene fragment. Doppler profiles were measured for various orientations of the electric vector of the pump laser and the directions of propagation of both the pump and probe lasers. Equivalent Doppler profiles, of 0.060 cm^{-1} FWHM, were obtained for NO products under all conditions. This observation requires the distribution of NO velocities to be spatially isotropic, i.e, not aligned with respect to the pump laser electric vector. Similar spatial flux isotropy was reported for the ν_7 predissociation of the ethylene dimer; spatially anisotropic flux distributions have however been reported for prompt photodissociation processes. Real time measurements of the appearance of the NO fragment, in a dual laser pump/delayed laser probe experiment, proved that the lifetime of the vibrationally excited van der Waals complex was less than 10 ns. The isotropic flux suggests that the vibrationally excited complexes survive more than one rotational period. At the temperature of our beam, the average rotational period is ~ 35 psec., implying a lower limit of ~ 50 psec on the predissociation lifetime of the excited complexes.

In the vibrational predissociation of the nitric oxide dimer, following excitation by a frequency doubled short pulse CO_2 laser at 1870 cm^{-1} , the total distribution of available energy was determined. The rotational and spin-orbit states of both NO photofragments (for values of internal energy $< 426\text{ cm}^{-1}$), are described by a rotational temperature of 110 K. This corresponds to only 20% of the available excess energy going into rotational excitation of the two fragments in dramatic contrast to the results obtained on the ethylene dimer. The two lambda doublet states were observed to be statistically populated and the relative populations

of the two spin-orbit states were consistent with a spin-orbit temperature equal to the rotational temperature, indicating equilibration of the electronic spin- and nuclear rotation angular momenta in this reaction. This is an unusual instance, where a singlet parent dissociates to form two doublet state fragments since in previous examples (e.g., including CH_3ONO , HONO , and dimethyl methoxy phosphate) apparent selection rules favored one spin-orbit component. Real time measurements of the fragment appearance times indicated that the vibrationally excited complexes dissociate within 10 nsec. We determined the NO fragment flux to be spatially isotropic by measuring Doppler profiles at various experimental configurations. This is similar to our results on ethylene-NO and previous results on ethylene dimer and implies a lower limit on the predissociation lifetime of ~ 50 psec.

It is possible for us to probe the photodissociation dynamics of the NO-ethylene van der Waals complex following excitation to several different vibrational states. Of particular interest are the results following excitations at 1870 and 1900 cm^{-1} to either the NO stretch or the ethylene ($\nu_7+\nu_8$) combination band, respectively. Here there are several lower frequency vibrational modes that might act as receptors for the available excess energy -- on the order of 1500 cm^{-1} . These mode specific experiments are in progress. In addition, experiments are in the planning stages (see section F) to determine the lifetimes of these vibrationally excited species using psec lasers for excitation and probing.

E. Matrix Isolation Spectroscopy (M. E. Jacox)

The assembly and testing of the vacuum systems and the cryogenic cell for use with the high resolution Bomem interferometer have been completed. Experimental studies using this apparatus are scheduled to begin in September.

With the help of Dr. Thomas Buckley, Chemical Thermodynamics Division, and Mr. Ricardo Metz, a summer worker in the Chemical Kinetics Division, substantial progress has been made in the software development for use with the Ebert visible-ultraviolet scanning monochromator. As this is written, it is planned to resume the long-suspended studies of the ultraviolet absorption spectra of transient molecules in the near future. The work is supported by ARO.

1. Fluorine-Atom Reactions

A major effort was the preparation of a review paper, entitled "Spectroscopy and Photochemistry of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," which has recently been published in Reviews of Chemical Intermediates. This paper provides a comprehensive review of both gas-phase and matrix isolation studies of the various types of F-atom reactions (e.g., addition, H-atom abstraction) which have yielded spectroscopic or photochemical data for the primary free radical products.

Because hydrogen-atom abstraction from a generalized molecule, RH, in an argon matrix leads to the formation of hydrogen-bonded $R\cdots HF$, this review has included an assessment of the extent of perturbation of the HF-stretching vibration of $R\cdots HF$ species which results from trapping of the complex in an argon matrix. Also included is a summary of shifts in the molecular vibrations, observed in solid argon, upon hydrogen-bonding of various types of molecules with HF.

Studies of the reaction of F atoms with methyl chloride, bromide, and iodide were completed. Evidence was obtained for a steric effect on the mechanism of F-atom reaction with these molecules, with two major reaction channels for each system. Attack of the F atom at the halogen position results in the formation of the CH_3XF addition product, which has a moderately strong X-F bond and is photochemically stable at wavelengths as short as 250 nm. F-atom reaction with a hydrogen atom of the methyl halide results in the stabilization of a weakly bound $F\cdots HCH_2X$ complex, intermediate to the formation of $H_2CX\cdots HF$ in the solid. For all of the species studied except CH_3Cl , the barrier to the decomposition of this complex is sufficiently great to require exposure of the solid deposit to visible light for the production of $H_2CX\cdots HF$. A paper presenting these results in detail is scheduled to appear in an October issue of Journal of Chemical Physics.

Studies of the reaction of F atoms with formic acid were initiated, with the objectives of determining whether the H-CO₂ structure has a ground-state potential minimum and of obtaining the spectra of the important combustion intermediates cis- and trans-HOCO in solid argon. (Previous studies in this laboratory had yielded the infrared spectra of these two species in solid CO, with which HOCO would be expected to hydrogen-bond.) Although some of the isotopic substitution studies, useful for a final normal coordinate analysis, remain to be completed, the following conclusions are evident:

- (1) If the H-CO₂ structure has a ground-state potential minimum, it is formed with too much energy for stabilization in this system.
- (2) Evidence for the formation of an $HCOOH\cdots F$ intermediate when the F atom attacks the OH bond of HCOOH is provided by the appearance of a high yield of $CO_2\cdots HF$, with little evidence for isolated CO_2 , in the initial deposit.
- (3) F atoms abstract H directly from the C-H bond of HCOOH, leading to the stabilization of isolated HOCO, as well as of $HOCO\cdots HF$.
- (4) Trans-HOCO is more stable than the cis-rotamer.

Preliminary studies of the important $F + SiH_4$ reaction system indicated that extensive reaction occurs.

2. Excited Rare-Gas Atom Reaction

The interaction of excited argon atoms with formic acid was found to lead to the stabilization of trans-HOCO in solid argon. Studies of this reaction system were extremely valuable in the detailed assignment of absorptions in the corresponding F-atom reaction study to isolated HOCO and to HOCO...HF.

The interaction of excited argon atoms with silane was found to provide a relatively "clean" yield of SiH₂, with only weak contributions of other products to the observed infrared spectrum.

3. Vibrational and Electronic Energy Levels of Transient Molecules

A paper entitled "Ground-State Vibrational Energy Levels of Polyatomic Transient Molecules," summarizing both gas-phase and inert matrix data for almost 500 species containing from 3 to 16 atoms, was published in the October 1984 issue of the Journal of Physical and Chemical Reference Data. In keeping with the rapid pace of new developments in this field, on May 1 a supplement containing data for 76 molecules which had appeared in the literature since August 15, 1984, was prepared for distribution with the reprints. An up-to-date digital record of developments in this fast-moving field is being maintained, and in one or two years it is planned to publish a supplement.

A proposal entitled "Spectroscopic Properties of Excited Electronic States of Small Polyatomic Transient Molecules" was submitted to the Office of Standard Reference Data, and beginning on September 1 will be supported for a period of two years. The output of this project will be a critically evaluated compilation of the experimentally determined spectroscopic properties of the bound and dissociative excited electronic states of covalently bonded transient molecules containing from three to six atoms. Spectroscopic data observed for transient molecules in the gas phase and in dilute solid solution in the rare gases or in non-polar small-molecule solvents will be included. The extent of deviation of the transition origins, vibrational fundamental frequencies, and radiative lifetimes of transient molecules observed in these media from the values reported for the gas-phase species will be assessed, in order to provide an estimate of the expected deviations for molecules for which gas-phase data are not available.

4. Reaction Intermediates in the Decomposition of Energetic Materials

With support from the Army Research Office, studies of the infrared and ultraviolet spectra of reaction intermediates derived from the decomposition of benzene and nitrobenzene are being pursued. Spectroscopic identifications are also being sought for a number of other small free radicals which play important roles in the decomposition of explosive or propellant molecules.

Preliminary infrared studies have been made of the photodecomposition of benzene isolated in solid argon by 254-, 122-, and 105-107-nm radiation. There is evidence for the stabilization of at least four products: phenyl radical, benzyne (C_6H_4), and two or more other species, one of which photodecomposes when the sample is exposed to the full light of the medium-pressure mercury arc.

Preliminary studies were also conducted of the photodecomposition of nitrobenzene isolated in solid argon, using the highly dilute Ar:nitrobenzene = 2000 samples which could be prepared in a conventional sampling system. Photolysis sources were 254-nm mercury-arc radiation and a beam of excited argon atoms, which provides a source of energy in the 11.5-11.8 eV range. Infrared absorptions of new products did not appear in either system. Previous studies had indicated that in the 254-nm spectral region the most important photodecomposition process is O-atom detachment, but that some NO_2 is also produced. No photodecomposition products were detected in the preliminary experiments. Since O atoms can diffuse from the site of their photoproduction in solid argon, failure to detect nitrosobenzene or O-atom reaction products suggests that previous studies may have overestimated the extent of O-atom photodetachment in the primary decomposition of nitrobenzene. Phenyl radical and NO_2 , products of the other primary photodecomposition process, would be expected to undergo cage recombination to re-form nitrobenzene or, possibly, to form the previously unobserved species phenyl nitrite. The negative results obtained in these preliminary studies are most consistent with the formation and recombination of phenyl radical and NO_2 . Experiments with more concentrated nitrobenzene samples will be necessary in order definitively to exclude the formation of nitrosobenzene and/or phenyl nitrite under these conditions. Construction of an auxiliary vacuum manifold to permit higher concentration studies of low vapor pressure materials is in progress.

In a search for infrared absorptions of the H_2CN free radical, which may play an important role in the decomposition of RDX and HMX, studies of the infrared spectra of the products of the $H + HCN$ reaction were initiated, using a microwave discharge through an Ar: H_2 mixture as the H-atom source. Rather weak infrared absorptions of CN and of three other products were detected. Positive identification of these three products, which differ in their photodecomposition thresholds on exposure of the sample to filtered mercury-arc radiation, must await the completion of planned isotopic substitution studies.

F. Future Plans

1. Condensed Phase Energy Transfer

The most significant questions for us to answer in the area of energy transfer for molecules on surfaces are: (1) What is T_1 , for a molecule on a metal surface? (2) What are the pathways of energy transfer (i.e. where does the energy go)? (3) How is VET at surfaces related to chemistry? Experiments are planned to answer these questions.

We have measured vibrational relaxation rates for high frequency vibrations on dielectric surfaces at the solid/vacuum and solid/liquid interface, in liquids, in amorphous and crystalline dielectric solids. We do not have one simple theory to interpret all the results in a consistent fashion. It appears qualitatively that one may interpret all the results in simple terms of masses connected by springs. However for vibrational relaxation on a metal surface, it is thought that a qualitatively different energy transfer mechanism, damping by excitation of electron-hole pairs in the metal, may be dominant. If this is true, then perhaps the broad spectral linewidths observed for high frequency vibrations on metals really are due to T_1 broadening as has often been assumed. A direct time resolved measurement of vibrational relaxation for a molecule on a metal surface is crucial to assessing the importance of this damping mechanism, and for understanding surface spectroscopy and kinetics.

We have several different strategies for measuring T_1 for a molecule on a metal surface. One approach is to perform our usual one color IR pump/probe time-resolved bleaching experiment for molecules on supported metal clusters. Another approach is to use the same technique for ordered monolayers on large metal single crystals under UHV conditions. A third approach involves IR excitation of a molecule bound to the surface of a metal (e.g. Au) particle suspended in liquid as a sol; this would be followed by anti-Stokes Raman scattering (surface enhanced) as a time dependent probe of vibrational population. These experiments require infrared laser pulses of suitable energy, bandwidth, frequency, and duration. The present Nd-Yag pumped OPA setup has several important limitations. Only frequencies $\nu_{IR} > 2600 \text{ cm}^{-1}$ can be generated, which restricts us to high frequency vibrations. However, because of its large transition dipole moment, and because of the wealth of surface information available, we want to study CO on metals. This requires $\nu_{IR} \approx 2000 \text{ cm}^{-1}$, not possible with the present setup. Also, the pulse duration of 15-20 ps with the present system is too long for many experiments (e.g. NH_2 on SiO_2 , and probably CO on metals). The broad spectral bandwidth from the OPA is also undesirable for many reasons (e.g., for the experiment to work an extremely large anharmonicity is required).

Therefore, in future T_1 experiments we will produce tunable IR radiation by generating the difference frequency, $\omega_{IR} = \omega_1 - \omega_2$, between two visible laser pulses in non-linear crystals. For frequencies $\omega_{IR} \geq 1800 \text{ cm}^{-1}$ we will use LiIO_3 and for lower frequencies $900 < \omega_{IR} < 1800$ we have tried AgGaS_2 . We are trying two approaches to generate the necessary visible pulses to be used for mixing. At a 20 Hz repetition rate we will amplify the outputs of both synch-pumped tunable dye lasers so that each has an energy of 0.5 mJ/pulse (as of 7/85 one of the two necessary amplifiers was operational). An alternative is to double the $\text{Nd}^{+3}:\text{YAG}$ light to synchronously pump a dye laser cavity. The dye laser output should be of significantly shorter duration than the 532 nm pumping pulses. The tunable IR, generated by difference frequency mixing ($\omega_{IR} = \omega_{532} - \omega_{\text{dye}}$) should have the duration of the input dye pulse. Both

difference frequency schemes should be capable of generating 1-10 μJ pulses in the 5 μm region. This should be sufficient to perform experiments described below.

It is conceptually straightforward to do the one color IR pump/probe transmission IR experiment to measure T_1 for CO ($v=1$, $\omega=2000\text{ cm}^{-1}$) on dispersed Pt particles supported on a SiO_2 disk. The transmission IR spectra of such samples have been extensively studied over the last 30 years. During the past year we have attempted this type of experiment for higher frequency vibrations ($3000-4000\text{ cm}^{-1}$) of molecules chemisorbed on dispersed metals (M-OH, M-NH, M-C₂H₂) without success. Two major problems - sample damage by the pump pulse and excessive scattering of pump light into the probe detector - have been solved by improved sample preparation. However, it is difficult to chemisorb these species in sufficient concentrations for study. Previous work shows that this should not be a problem for CO on metal surfaces. Also, molecules which absorb in the high frequency range tend to have relatively low vibrational transition dipole moments compared to CO chemisorbed on metals. Thus CO/metal systems offer important advantages. We expect in 1986 to perform the simple pump/probe experiments to measure T_1 for CO($v=1$) bound to a variety of dispersed supported metals.

In principle the IR transient saturation experiment is applicable to any sample for which ordinary IR absorption spectroscopy is possible, including monolayers on metal single crystals. For most vibrations on single crystals, infrared reflection-absorption spectroscopy (IRAS) requires the detection of very small absorptions, typically 2×10^{-4} . With our present detectors and poorly behaved OPA pulses, we can only detect transmission changes greater than 0.3%; to determine the slope of the $\ln(T/T_0)$ plot (i.e. T_1) presently requires a change in T (caused by the pump) of at least 1.5%. The present apparatus thus has two orders of magnitudes less sensitivity than that necessary to measure T_1 for typical surface vibrations. We expect that our sensitivity can be significantly improved since other laboratories have claimed 1 part in 10^5 using pulsed lasers. In fact, for CO on metals, sensitivity limitations are not as severe since absorptions of 1-2% are usually reported in IRAS experiments. We are working toward attempting to measure T_1 for CO on Pt(111) or related metal single crystal surfaces using the IR pump/probe method. Better laser pulses, better pulsed IR detection and signal averaging, and significant additional surface preparation and characterization (e.g. high resolution IRAS capability) equipment will be needed.

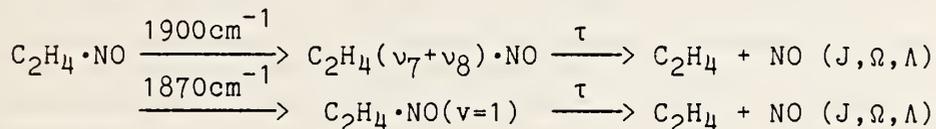
A direct measurement of the pathways (accepting modes) involved in the VET experiments requires a determination of population in different sample vibrational modes. Time-dependent Raman or IR spectroscopy may be used. For samples of good optical quality, such as colloidal silica particles suspended in CCl_4 , or for the liquid samples of $\text{R}_3\text{Si-OH}$ molecules (which may be models for the surface vibrations), we will perform IR pump/SPARS probe experiments (using either OPA/532 nm or IR difference frequency systems) in 1986. To decrease background signals from the thermal population in very low energy modes the samples may be

cooled (as done for the CS₂ T₂ experiments). It is likely that other samples (pressed disks, dispersed supported metals) will scatter too much visible light to permit detection of the expected weak SPARS signals. For these samples 2 color IR transmission spectroscopy (pump one mode, probe another) may be used. This approach is likely to be successful only for a few surface species where energy flows from one high frequency vibration to a neighboring high frequency mode before dissipating to the low frequency ($\nu < 1200 \text{ cm}^{-1}$) lattice modes. As an alternative to SPARS probing of vibrational population (e.g. OH $\nu=1$), we may try CARS probing. The CARS method has the advantage of generating more detected signal photons per pulse, but the disadvantage of requiring large excited state densities and three coincident laser pulses.

To date our surface T₁ measurements have been for molecules on collidal SiO₂, a surface which has little catalytic activity. One way we hope to explore the relation between VET and surface chemistry is to study T₁ for systems with important catalytic activity. For instance, the hydroxyl groups inside zeolite catalysts are associated with active Brönsted acid sites, and there have been many transmission IR studies of these OH sites in the 3700 cm⁻¹ region. In collaboration with Dr. R. Wormsbecher at W. R. Grace (Columbia, MD) we hope to measure T₁ times for OH stretching vibrations in a number of zeolites of different catalytic activity.

2. Dynamics of van der Waals Molecules

The same synch-pumped picosecond laser apparatus which will generate IR pulses suitable for studying VET rates for bonds on metal surfaces, will also generate pulses suitable for doing VET studies involving the photodissociation of van der Waals molecules. An example of a van der Waals experiment which we should do in 1986 is the photodissociation of NO·C₂H₄ by $\nu_{\text{IR}} \approx 1900 \text{ cm}^{-1}$



There is a significant controversy about the value of τ , the predissociation lifetime. The photodissociation spectrum in the C₂H₄ ν_7 region is a Lorentzian (FWHM = 6cm⁻¹), which has been interpreted as implying $\tau = 0.9 \text{ ps}$. Our time-resolved measurements of product appearance using nanosecond lasers proved that $\tau < 10 \text{ ns}$. However our measurement of isotropic flux distribution suggested that $\tau \geq \tau_r$, where the rotational time of NO·C₂H₄ in our beam is $\tau_r = 35 \text{ ps}$.

We will generate tunable IR at 1900 or 1870 cm⁻¹ by generating the difference frequency in LiIO₃ of the two amplified synch-pumped lasers. One of them (at $\lambda = 575 \text{ nm}$) is frequency doubled; the $\lambda = 288 \text{ nm}$ is summed with Nd-Yag (1.06 μm) in a KD*P crystal to generate light at 226 nm (P₁ head = 44176 cm⁻¹) suitable for LEF detection of the NO photoproduct on

the $\tilde{A} \leftarrow \tilde{X}$ transition. Measurement of the NO LEF signal vs. pump/probe delay time (t_D), will determine τ for excitation of $C_2H_4(v_7+v_8) \cdot NO$ at 1900 cm^{-1} compared to $C_2H_4 \cdot NO(v=1)$ at 1870 cm^{-1} . It will be interesting to see if the product yield has an exponential build-up as $NO(t) = [1 - \exp(-t/\tau)]$, as predicted by statistical theories, and to see if there is any relationship between τ and photodissociation line widths. Excitation of the out-of-plane v_7 motion which corresponds to the reaction coordinate, may give a short τ , while there may be a significantly longer time for NO stretching energy to flow into the van der Waals bond leading to dissociation. Similar experiments are planned in which C-H stretching modes of van der Waals clusters will be excited with picosecond IR pulses. The necessary $3 \mu\text{m}$ light will be produced by the same dye lasers by difference frequency generation.

3. Desorption of Molecules from Surfaces

Several years ago we undertook a joint research project involving staff and expertise of the Molecular Spectroscopy and Surface Science Divisions of the Center for Chemical Physics to examine in greater detail molecular dynamics at the gas-surface interface. The thrust of this program was to use laser based, state and velocity selective diagnostics to study molecules being thermally desorbed from well-characterized single crystal metal surfaces in an ultra high vacuum environment. The results of our work on NO/Ru(001) and NO/Pt(111) have been published and are reviewed herein. What is important about these experiments is that they are extremely, perhaps uniquely, sensitive to the interactions between gas molecules and different metallic surfaces.

The future directions of this research effort can be broken up into two branches. First, in view of the marked differences for NO/Pt, where there is only simple molecular desorption, versus Ru, where decomposition competes with desorption, during FY'86 we plan to explore the desorption of NO from 1) co-adsorbed layers of NO and ammonia on Pt(111) where there appears to be a co-operative interaction during the desorption process; and 2) Ir(111) where a major source of the desorbing NO is from atom-atom recombination. Although all our present work has emphasized interactions with the NO adsorbate, we hope to acquire a second dye laser to enable us to extend our laser probe capabilities into the vacuum ultra-violet and study the molecule-surface dynamics of other, chemically interesting species such as hydrogen and CO.

Thermal desorption studies are sensitive to the molecular dynamics and energy flow in the region of the top of the chemisorption potential energy well - a region important in the making and breaking of chemical bonds. In the thermal desorption experiment the heating rates traditionally used are much slower (e.g. 10 K/sec.) than other molecular relaxation processes, which is good if one's goal is to study the dynamics of a highly energetic system under "equilibrium" conditions. A deeper level of understanding can be obtained regarding molecule-surface energy transfer by attempting to study non-equilibrium conditions, such as might be achieved following laser irradiation of the adsorbate covered surface.

We hope during FY'86 to successfully characterize the internal state distributions, kinetic energy and angular flux distributions of the NO driven off a Pt(111) surface by non-resonant laser excitation at 532 nm. Estimates of the anticipated signal levels for desorption of 10^{-4} of a monolayer per laser shot indicate that we should be able to determine the vibrational as well as rotational partition functions. These experimental results will provide a stringent test of the theoretical treatments currently being applied to model laser-surface heating and energy transfer processes.

4. Matrix Isolation Studies

The high sensitivity and extended spectral range afforded by the Bomem interferometer will be crucial to the study of a number of important systems during the coming year. Among the first systems to be studied will be the photodecomposition of acetylene to produce HC_2 and C_2^- . Electronic transitions for both have recently been reported near 4000 cm^{-1} . Observation of the absorptions resulting from these electronic transitions in a rare-gas matrix will aid in the definitive identification of the C_2^- transition and in the assignment of the bands arising from vibrationally unexcited HC_2 , which has an unusually low ground-state bending vibrational frequency.

Priority will also be given to the studies of the $\text{H} + \text{HCN}$ reaction, in which the greater sensitivity of the Bomem interferometer will be valuable for the definitive assignment of the infrared spectra of H_2CN and of cis- and trans- HCNH . A search will also be made for near infrared transitions of these species, each of which, like the isoelectronic species HCO , may have a low-lying electronic transition.

As reported one year ago, the feasibility of detecting the infrared and electronic spectra of molecular ions produced by codepositing a beam of excited neon atoms with a suitable precursor molecule isolated in solid neon has been demonstrated. The energy range accessible using excited neon atoms (16.6-16.8 eV) will substantially broaden the range of molecules whose ions are accessible over that covered in earlier experiments in this laboratory using excited argon atoms, permitting a search for such important ions as HCO^+ , H_2O^+ , NH_3^+ , and CH_4^+ . These long-planned studies have been deferred until they could be conducted on the Bomem interferometer, since the enhanced sensitivity of this instrument is especially important when liquid helium must be used as the coolant. It is hoped that studies of these experiential systems can proceed during FY'86. Such studies may provide much previously inaccessible information on the vibrational and electronic spectra of molecular ions, important in a variety of high energy systems ranging from combustion to high-speed flight.

The higher sensitivity of the Bomem interferometer will permit studies of such other important classes of molecule as carbon-13 substituted species present in natural abundance and products of O-atom reactions in discharge sampling experiments. Observations of the

carbon-13 species will aid in product identification and will provide valuable data for infrared spectral analysis. Since water and oxygen impurities generally lead to the formation of O atoms in discharge sampling experiments, the greater sensitivity of the Bomen inteferometer will both facilitate and mandate a series of studies of the reactions of O atoms with small molecules. Such studies of the reactions of O atoms with benzene and with nitrobenzene form an important part of the current program of research being supported by the Army Research Office.

Preliminary studies have indicated that species of formula HCN_2 are stabilized by the reaction of photochemically generated CH with a nitrogen matrix. Further studies will be conducted in order to obtain a definitive identification of this product, which may play important roles in processes as diverse as the decomposition of explosive or propellant molecules and the generation of "prompt" NO on atmospheric combustion of hydrocarbons.

In order to obtain as complete as possible a characterization of the spectra of the products of elementary reactions of silane, studies will be continued not only on the reaction of excited argon atoms and of F atoms with silane, but also on the corresponding H-, Cl- and O-atom reactions.

Because F-atom reaction studies have provided an extremely valuable tool for obtaining free radical spectra, they will continue. Emphasis will be placed on studies of the ultraviolet absorption spectra of the products of F-atom reaction with such species as CH_3NO_2 , CH_3CHO , CH_3CN , and HCOOH , for which infrared studies have provided definitive identifications of free radicals.

As it becomes possible to stabilize a wide variety of molecular ions and O-atom reaction products in rare-gas matrices, it will be increasingly important to determine their laser-excited fluorescence spectra, in order to provide a more complete characterization of their energy levels and to establish a basis for their detection in atmospheric and combustion systems. This need will mandate construction of a laser-excited fluorescence system dedicated to matrix isolation studies. This system will also permit unique experiments to determine previously inaccessible low-lying molecular electronic states; cage recombination of molecular fragments formed on laser photodissociation of the matrix-isolated molecule may populate such low-lying states, which may then be deactivated by fluorescence or phosphorescence.

4. QUANTUM CHEMISTRY GROUP

H. Basch, P. Jasien, P. S. Julienne, M. Krauss,
F. H. Mies and W. J. Stevens

A. Introduction

Atomic and molecular electronic structure and scattering methods are developed and applied to chemical and spectroscopic problems where experiments are difficult to perform or so complicated that the theory is needed to model the results.

The electronic structure method and code development and applications now include chemical problems with large molecular systems including models of biomolecules. The applications to the biotechnology area utilize the recently acquired IBM-4381 in the Molecular Structure and Modeling Facility (MSMF) and are described in part in the competence summary.

B. Electronic Structure

1. Theoretical Proton Affinities (W. J. Stevens, P. Jasien)

A combination of several state-of-the-art ab initio quantum chemistry methods has been applied to the quantitative determination of the proton affinities of small molecules containing the Group VI elements, O, S, Se, and Te. Several series of molecules have been studied including CX, CX₂, OCX, and H₂CX (where X is the Group VI atom). Comparisons with available experimental data are very good, and the estimated accuracy of the theoretical results is ± 2.5 kcal/mole. These are the first such accurate calculations ever carried out for compounds containing selenium and tellurium. In addition to the proton affinities, trends down the Periodic Table are now available for favored protonation sites, vibrational frequency shifts upon protonation, and structural distortions due to protonation.

Compact effective potentials (CEP), which were developed at NBS, allow the chemically unimportant core electrons to be eliminated from the molecular wavefunctions with little loss of accuracy. Thus, all of the Group VI elements were treated as six electron atoms. Relativistic effects are incorporated through the use of Dirac-Fock atomic wavefunctions in the determination of the core potentials.

Full analytic energy gradient geometry optimizations of all neutral and protonated species were carried out at the single configuration self-consistent-field (SCF) level using accurate "double-zeta plus polarization" basis sets. At the optimized geometries, harmonic force constants were determined from numerical first derivatives of the analytic energy gradients, and zero-point vibrational energy contributions to the proton affinities were calculated. Electron correlation energy contributions were evaluated by configuration interaction calculations including all single and double excitations from the single configuration SCF wavefunctions.

This work is described in: P. G. Jasien and W. J. Stevens, J. Chem. Phys. 83, 2984 (1985).

2. Hydrogen Bonding of Water and Methanol with Formamide (W. J. Stevens and P. Jasien)

The characterization of the hydrogen bonding between water and formamide has been of considerable interest to experimentalists and theoreticians alike. This interest stems from the fact that formamide may be viewed as the simplest molecule containing a peptide linkage. As such, the formamide-water complex provides the simplest model for the hydration of proteins.

We have carried out detailed calculations on several conformers of the formamide-water complex at a level of accuracy significantly beyond all previous theoretical studies. Full gradient energy optimizations using double-zeta plus polarization basis sets were carried out for each conformer. The effects of electron correlation were determined by configuration interaction including all single and double excitations from the SCF configuration.

These accurate calculations show hydrogen bonding of water to the carbonyl group to be favored by about 0.5 kcal/mol over bonding to the amide group. However, a cyclic structure in which the water is hydrogen bonded to the carbonyl and amide groups simultaneously is found to be most stable (9.5 kcal/mol) and is a likely candidate for molecular beam microwave spectroscopic studies.

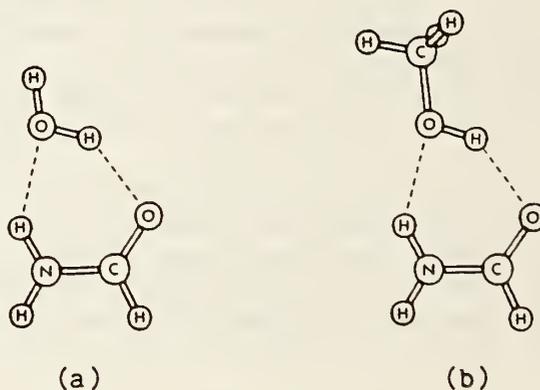


Fig. 4.1. Most stable hydrogen-bonded complexes of (a) water-formamide and (b) methanol-formamide illustrating near coincidence of the two structures.

Calculations were also carried out on methanol-formamide complexes to determine if any fundamental differences exist in the hydrogen bonding of the alcohol versus the water. The results show virtually identical structural

and energetic behavior of the methanol-formamide complexes when compared to the water-formamide complexes. Again, the cyclic, doubly hydrogen-bonded conformer is the most stable. Figure 4.1 shows the striking similarity of the two cyclic structures.

The systematic study of basis sets, geometry optimizations, and correlation energy for these hydrogen bonded complexes have allowed us to set up general guidelines for future calculations of this type.

3. Localized Electron Pair Polarizabilities

(W. J. Stevens, P. Jasien)

The coupled, perturbed Hartree-Fock method (CPHF) has been used to calculate the dipole polarizabilities of several prototypical non-aromatic molecules containing H, C, O, and N. The list of molecules studied and the principal components of their calculated polarizability tensors are shown in Table 4.1. All calculations were carried out with triple-zeta basis sets augmented by two polarization functions on each atomic center. The resulting polarizabilities are very close to the Hartree-Fock limit of accuracy, which is generally within 15% of experimental values for the isotropic part.

It is possible to transform the Hartree-Fock molecular orbitals, via a unitary transformation, into localized orbitals that can be identified as bonds and lone pairs. The same unitary transformation may be applied to the orbital components of the CPHF molecular polarizability. In this way, electron-pair polarizability tensors may be derived that are transferable from molecule to molecule. Preliminary transferability studies have been made using average bond and lone pair polarizabilities extracted from the saturated molecules listed in Table 4.1. Table 4.2 compares spherically averaged CPHF polarizabilities to polarizabilities obtained as a sum of transferable bond and lone pair components. The agreement is within a few percent. Anisotropic behavior and unsaturated bonds are still under investigation but show similar promise. A functional group analysis (e.g. methyl group, hydroxyl group, amide group) may be required in order to take full advantage of anisotropic tensor contributions.

Transferable polarizabilities are a key ingredient in the ab initio reaction field method being developed by the Quantum Chemistry Group. A reaction field computer code will allow the study of very large molecular systems by treating a small portion fully quantum mechanically while representing the surrounding environment by a distribution of polarizable point multipoles. The distribution of the point multipoles and their polarizabilities will be determined from ab initio calculations on prototypical molecules and fragments whose properties are assumed to be transferable.

Table 4.1. Ab initio CPHF polarizabilities and selected experimental values for comparison (in Å³).

Molecule		α_1	α_2	α_3	$\bar{\alpha}$
H ₂ O	CPHF	1.21	1.34	1.10	1.22
	EXP	—	—	—	1.49
NH ₃	CPHF	1.89	1.85	1.85	1.87
CH ₄	CPHF	2.37	2.37	2.37	2.37
	EXP	2.62	2.62	2.62	2.62
HCN	CPHF	3.30	2.00	2.00	2.43
H ₂ CO	CPHF	3.13	2.39	1.77	2.43
	EXP	2.76	2.76	1.83	2.45
HCCH	CPHF	4.62	2.78	2.78	3.39
C ₂ H ₄	CPHF	5.25	3.68	3.27	4.07
C ₂ H ₆	CPHF	4.31	3.83	3.83	3.99
	EXP	4.99	4.22	4.22	4.48
CH ₂ NH	CPHF	4.29	3.01	2.42	3.24
CH ₃ OH	CPHF	3.13	2.85	2.64	2.87
	EXP	4.09	3.23	2.65	3.32
CH ₃ NH ₂	CPHF	3.90	3.36	3.35	3.54
C ₂ H ₅ OH	CPHF	4.97	4.64	4.13	4.58
	EXP	5.76	4.98	4.50	5.08
CH ₃ OCH ₃	CPHF	5.16	4.41	4.18	4.58
	EXP	6.38	4.94	4.39	5.24
C ₃ H ₄	CPHF	7.31	4.27	4.27	5.29
C ₃ H ₆	CPHF	7.39	5.30	4.62	5.77
CH ₃ CN	CPHF	5.61	3.50	3.50	4.20
	EXP	5.74	3.85	3.85	4.48
CH ₃ CHO	CPHF	4.92	4.07	3.31	4.10
C ₃ H ₈	CPHF	6.17	5.57	5.32	5.68
	EXP	7.66	5.74	5.74	6.38
NH ₂ CHO	CPHF	4.63	3.57	2.66	3.62
	EXP	5.24	$\alpha_2 + \alpha_3 = 7.01$		4.08

Table 4.2. A comparison of CPHF molecular polarizabilities and polarizabilities constructed from transferrable average bond and lone-pair contributions.

Molecule	$\bar{\alpha}_{\text{CPHF}}(\text{\AA}^3)$	$\bar{\alpha}_{\text{TRANS}}(\text{\AA}^3)$
CH ₄	2.28	2.27
CH ₃ OH	2.87	2.98
C ₂ H ₅ OH	4.58	4.63
C ₂ H ₆	3.99	3.95
C ₃ H ₈	5.68	5.62
C ₂ H ₆ O	4.58	4.73

4. Binding of Pt Complexes to DNA (H. Basch, M. Krauss, W. J. Stevens)

The binding of the Pt diamine moiety to DNA was found to occur predominantly in a cis intrastrand chelate between neighboring guanine bases. The stereospecificity of the binding was recently called into question by the observation of anti-tumor properties for both cis and trans Pt diammine ascorbate molecules. Calculations of the relative trans effects and binding energies for the carbon and oxygen ligand binding sites have shown that the carbon site is less labile than the ammonia ligand. As a result cis chelates can be formed with the DNA in reaction with either the cis or trans Pt ascorbate molecules.

Substituted amines have also been considered in the binding of Pt(R-NH₂)₂²⁺ to one or two imidazole ligands. The imidazole is used to model the N7 binding site in guanine. The binding energies for R=CH₃ or cyclopropyl are found to each reduce in turn by 6% from the unsubstituted values for R=H. These relatively slight variations in binding energy are not expected to play a role in the binding behavior of the substituted Pt amines to DNA. Steric effects are now being modeled to analyze the effect of the aliphatic substitution. Preliminary results indicate that steric effects are not significant for R = CH₃ or cyclopropyl. This work is supported by the National Foundation for Cancer Research.

were added to all heavy atoms except the two methyl carbons. The second GLY conformer was then found to be lowest in energy. This result can be rationalized in terms of the importance of H-bonding in the conformers. The GLY-1 conformer contains a seven member ring with the amide hydrogen of one amide group bonded to the carbonyl oxygen in the other amide group. Double zeta calculations have been found to overestimate H-binding, and adding polarization functions provides lower and more accurate SCF values.

The comparison with the ECEPP energy orderings is not as good. However, comparison with an empirical method requires the evaluation of the dispersion interaction. Simple London type dispersion calculations for all non-bonded interactions shows very little variation with conformation. For example, the dispersion energy difference between the C1, C2, and C6 conformers of GLY is less than 0.2 kcal/mole. More accurate analyses of the correlation energy are sufficiently difficult that this estimate suggests much effort would not be rewarded. The discrepancy with classical energetics at specific conformers is likely to remain. Whether the topography of a ψ , ϕ map will be qualitatively different, needs to be explored for specific dipeptides.

Table 4.3. Comparison of Dipeptide Conformer Energetics Energy (kcal/mole)

Peptide	Conformer	DZ	DZP	Ref. 1	Ref. 2	Ref. 3
GLY	QM1	0.0	0.5		0.0	0.0
	QM2	0.02	0.0		0.8	0.8
	QM3	4.5	3.8		4.7	1.0
	QM4	4.0	3.2		4.3	1.2
	C1	0.3		0.0		
	C2	0.0		0.7		
	C6	8.7		1.7		
	C8	7.7		5.1		
ALA	QM1	0.0			0.0	0.0
	QM2	0.5			1.4	0.4
	QM3	2.6			2.6	8.8
SER	C1	0.0		0.0		
	C2	3.8		1.2		
CYS	C1	0.0		0.0		
	C3	4.2		0.2		
ASP	C1	2.8		0.0		
	C3	0.0		0.3		

1. Calculations with ECEPP; communicated by S. Chin, Kingston, IBM.
2. J. N. Scarsdale, C. V. Alsenoy, V. J. Klimkowski, L. Schäfer, and F. A. Momany, *J. Chem. Phys.* 105, 3438 (1983).
3. S. S. Zimmerman, M. S. Pottle, G. Nemethy, and H. A. Scheraga, *Macromolecules* 10, 1 (1977).

C. Scattering in the Presence of Radiation

1. Radiative Redistribution

(P. Julienne)

We have continued close coupled scattering calculations to calculate the fine structure branching ratios to $^2P_{j=1/2}$ and $j=3/2$ when a Na atom is excited to a dissociative $^2\Sigma$ or $^2\Pi$ state during a collision with a rare gas perturber atom, He, Ne, or Ar. We have also predicted the alignment (orientation) of the $^2P_{j=3/2}$ atom if a linearly (circularly) polarized photon is absorbed. These calculations have been carried out in conjunction with Drs. Linda Vahala and Mark Havey of Old Dominion University, Norfolk, Va., and have successfully explained Dr. Havey's radiative redistribution experiments. These calculations and experiments study the molecular dynamics which occur between the time a photon is absorbed into a particular molecular state and the time it is re-emitted later as fluorescence. The nonadiabatic dynamics describe the way in which the coupling of orbital, spin, and nuclear rotation angular momenta changes as the excited atoms separate. This work is supported by AFOSR.

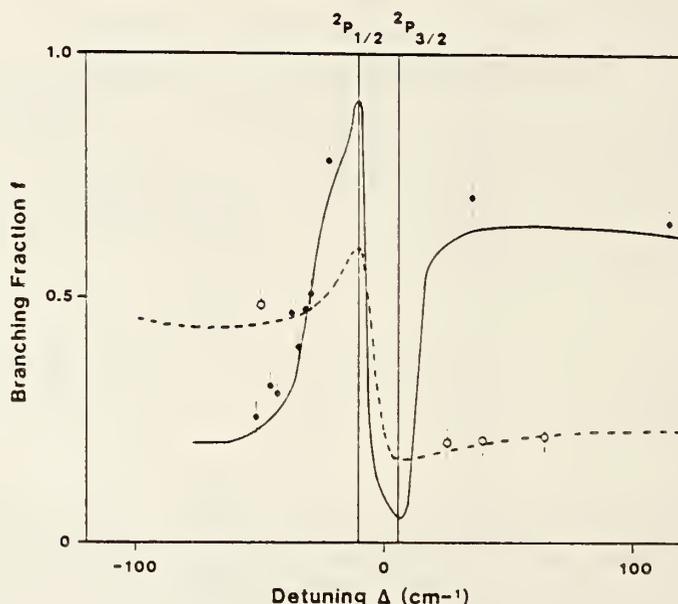


Fig. 4.2. Branching fraction f into Na $^2P(j=1/2)$ when Na $^2P_{j=3/2}$ or $1/2$ is produced following excitation of Na(2P) by photon absorption in the wings of the Na $^2P + ^2S$ transition broadened by collisions with Ar (solid line and filled circles) or He (dashed line and open circles). The detuning Δ is measured relative to the mean energy of the fine structure doublet. The lines give the results of close coupled scattering calculations using ab initio potentials. The points represent the measured values.

2. Application of Generalized Multichannel Quantum Defect Theory
(MCQDT)
(P. S. Julienne, F. H. Mies)

The generalized MCQDT applied to molecular potentials gives a way of relating the transition amplitudes for the closely related processes of photodissociation and radiative redistribution. The theory also permits, for suitable systems, the factorization of the transition amplitude matrix for both phenomena into separate factors representing short range Franck-Condon excitation and nonadiabatic final state interactions which occur at longer range and control the distribution of product states. We have tested this factorization for the $\text{Na}(^2\text{P}) + \text{rare gas}$ system studied above by applying the recoil limit for fine structure branching and polarization. The recoil limit for fine structure branching applies at sufficiently high fragment relative separation velocity, and was found to apply at much lower relative fragment kinetic energies for the light collision partner He than for Ar. Significant departures from the recoil limit apply at thermal energies, reflecting the influence of the molecular potentials on the nonadiabatic dynamics. An invited paper on the MCQDT analysis of molecular dissociation was presented at the International Conference on the Physics of Electronic and Atomic Collisions.

3. Product Distributions in Molecular Photodissociation
(P. S. Julienne and F. H. Mies)

For some time we have been using close coupled scattering calculations to calculate the nonadiabatic free-free redistribution phenomena. We are now generalizing our close coupling scattering codes to incorporate weak coupling to a bound state so we can calculate bound-free matrix elements for a final close coupled scattering state. This will enable us to calculate product distributions in molecular photodissociation. We have obtained the photodissociation code of Singer, Freed, and Band, and it is running on the University of Maryland VAX + FPS array processor computer system. We are currently implementing the renormalized Numerov algorithm of this code in our close coupling scattering code on the NBS CYBER 205 supercomputer. This work is supported by AFOSR.

4. Atomic Lineshapes and Resonance Fluorescence Spectra
(F. H. Mies and P. S. Julienne)

We are progressively expanding the capabilities of our close-coupled scattering codes to include many aspects of radiative coupling and laser-induced phenomena in molecular continuum spectroscopy. The programs incorporate the effects of non-adiabatic couplings and the resultant breakdown of the Born-Oppenheimer approximation. We directly extract the photon scattering cross-sections and redistribution spectra from the close-coupling codes, without any commitment to perturbation theory. Also we can systematically increase the intensity of the pumping laser field and achieve saturation. Our calculations yield the resultant non-linear response

of the absorption cross-sections in the presence of inelastic collisions. Further we have begun to incorporate two separate laser fields into our calculations. At present the second field is treated as weak and allows us to extract the resonance fluorescence spectrum in the presence of saturation by the pumping laser field. We are now calculating the pressure-broadened half-widths of the three peaked Mollow lineshape for the resonant transition in Sr. The following are four separate accomplishments associated with this program for FY85. This work is supported by AFOSR.

a. Continuum-continuum Matrix Elements in Atomic Lineshape Theory
(F. H. Mies and P. S. Julienne)

The calculation of the pressure-broadened lineshape for the atomic transition $A_i + h\omega_L \rightarrow A_f^*$ requires the evaluation of the following continuum-continuum matrix element

$$S_{fi}^{\text{rad}} = -i\pi \langle \psi_f^-(E^-) | \Omega_L | \psi_i^+(E^+) \rangle. \quad (1)$$

where the field-free multichannel wavefunctions ψ^\pm incorporate non-adiabatic effects and the breakdown of the usual Born-Oppenheimer Approximation. This expression applies in the weak-field limit, when the Rabi frequency Ω_L associated with the photon $h\omega_L$ is very small and when the radiative scattering matrix element S_{fi}^{rad} can be evaluated in perturbation theory. The precise details of the lineshape analysis depends on the extent to which the incident photon is detuned from the exact atomic resonance energy $h\omega_{fi}^0 = (E_f^* - E_i)$,

$$\Delta_{fi} = \omega_L - \omega_{fi}^0 \quad (2)$$

In the wings of the line, where Δ_{fi} is very large compared to the homogeneous width of the atomic transition, the absorption coefficient is directly proportional to the radiative scattering cross section determined by the transition matrix elements in Eq. (1). The impact approximation to the pressure-broadened half-width in the vicinity of the line center can also be expressed in terms of S_{fi}^{rad} .

For dipole allowed atomic transitions the radiative matrix element which defines the pressure-broadened atomic lineshape is only conditionally convergent. Using a commutator technique to redefine the integral we can isolate, and ultimately reject, the contribution of an indeterminate asymptotic surface integral which is associated with the energy normalization of the continuum wavefunctions which describe the binary collision of the atom and its perturber. The remaining contributions to the atomic lineshape are absolutely convergent. Since the transformed integrals apply as well to the multichannel wavefunction

they encompass the effects of non-adiabatic and inelastic scattering. Further we show the relationship of the commutator integral to the exact requirements of close-coupled scattering theory for radiatively-induced collisions. This scattering analysis suggests that we should interpret the convergent lineshape as an expression of multichannel inelastic collisions between field-dressed atomic states. The same interpretation applies both in the impact and the static limit. We would advocate that, since stable close-coupling codes are required to generate the multichannel wavefunctions in Eq. (1), it is a simple matter to merely expand the set of coupled equations to directly include the radiative coupling between channel states as required by the dressed atom boundary conditions and completely avoid explicit numerical quadrature of the multichannel matrix elements in Eq. (1).

b. Impact Limit in Weak Laser Fields
(F. H. Mies and P. S. Julienne)

Care must be taken when one attempts to apply the perturbation expression near the impact limit for allowed transitions. As the detunings $\Delta_{f,i}$, approach zero, the major contributions to the matrix element (1) occur in the asymptotic regions $R \rightarrow \infty$ and S_{fi}^{rad} becomes proportional to $1/\Delta_{f,i}$,

$$S_{fi}^{\text{rad}}(\Delta_{f,i} \rightarrow 0) \sim \sum_{f'} \sum_{i'} \frac{\langle \psi_{f'} | \Omega_r | \psi_{i'} \rangle}{2\Delta_{f',i'}} [S_{f',f'} \delta_{f',f'} S_{i',i'}] \quad (3)$$

This divergent limiting form is predicted by the impact theories of Shafer and Gordon and Ben-Reuven. In fact we can numerically extract this matrix element from the full close-coupling codes for small $\Delta_{f,i}$, and then employ these same impact theories to obtain accurate estimates of the collisional half-widths of pressure broadened lines. Note that the near resonance photon simultaneously causes a collective coupling among all the asymptotic channel states $\psi_{f,i}$, and $\psi_{i'}$, and we can never factor Eq. (3) into distinct products of initial and final state terms.

We have performed multichannel close-coupled calculations of the $\text{Sr}(^1\text{S}) \rightarrow \text{Sr}(^1\text{P})$ transition broadened by Ar. A comparison of the exact close-coupled radiative scattering matrix elements to eq. (3) confirms the validity and utility of our numerical procedures for obtaining pressure broadened half-widths in the weak field limit. This procedure should enjoy substantial application throughout lineshape theory.

c. Impact Limit and Pressure Broadening of Mollow Sidebands in Intense Fields
(F. H. Mies)

Our close-coupled procedures for evaluating S_{fi}^{rad} avoid any commitment to weak fields or perturbative estimates of S_{fi}^{rad} . Of course, in the weak field limit, we should choose a representative Rabi frequency sufficiently small to insure that Eq. (1) remains linearly proportional to Ω_L and yet sufficiently large to insure numerical accuracy of the close-coupled radiative scattering matrix elements. As long as the magnitude of S_{fi}^{rad} remains below about 10^{-3} there seems to be a one-to-one correspondence to Eqs. (1) and (3).

Of course true deviations from linearity must ultimately prevail as the actual field strength increases. Such effects become particularly important in the impact limit, and ultimately become manifest as pronounced sidebands in the fluorescence spectrum of the pressure-broadened atomic lineshape symmetrically located at frequencies $\pm\Omega_L$ from the scattered Raleigh line.

Experimental observations of the three-peaked Mollow lineshape have been made for Sr+Ar. We have made some preliminary calculations for Sr+Ar in the strong-field limit and confirm that our close-coupling procedures reproduce the dressing of the asymptotic Sr states and yields a three-level version of Eq. (3). We are now in the process of calculating the complete impact limit half-width for each of the separated peaks as well as the expected polarization properties of the intense field fluorescence.

In addition to the spectrum there have been experimental estimates (and semiclassical calculations) of the inelastic collisional energy transfer between the dressed Sr atomic states which causes collisional redistribution of the resonance fluorescence. These cross-sections are also being extracted from our calculations.

D. Multiphoton Effects in Resonance Fluorescence Spectra
(F. H. Mies)

Until now we have only allowed for a single photon transition in our close-coupled equations. In order to calculate the redistribution spectrum in intense fields we have introduced a second laser field with Rabi frequency Ω_p and frequency ω_p . So far we have only permitted a weak probe intensity Ω_p and have obtained a beautiful mapping of the Mollow lineshape for Sr+ Ar as a function of the probe detuning.

In view of our encouraging results with a weak probe field our ultimate goal is to also saturate this field and examine the close-coupled calculations for effects associated with four wave mixing. Again, such effects have been observed in Sr + Ar and we are confident that our techniques can derive reliable estimates of the appropriate cross-sections.

E. Future Plans

In the area of electronic structure calculations the Quantum Chemistry Group intends to move ahead in 1) the development of the reaction field methods and code, 2) the calculation of accurate prototype energy and properties for amides and nucleic acid components, and 3) model problems on H-bonding in enzymes, metal binding to both proteins and nucleic acids, and the analog behavior of phosphates and vandates in nucleus-substrate binding.

The reaction field development is the major thrust. As we improve the methods and the code we intend to apply the model calculations in category three to enzyme binding and spectroscopy problems. In the interim calculations in category two will provide insight into polarizabilities and dispersion interactions in large aromatic systems, the electronic structure of phosphorus and vanadium five-coordinate molecules, accurate hydrogen-bonding energies comparing H, O, and S sites, and metal binding to small amides and isolated nucleic acid bases.

Future plans in the scattering analysis call for further development and implementation on the CYBER 205 of efficient numerical algorithms for calculating accurate photodissociation transition amplitudes to a manifold of strongly coupled final states. Such codes enable us to calculate product state distributions following photodissociation. Initial calculations will be on diatomic systems with later generalization to small polyatomic systems. Specific calculations are planned for the NaK molecule in conjunction with experimental studies to be done at the University of Maryland. In addition to our numerical studies, we also will continue to develop an analytic half-collision theory of photodissociation and photo-assisted collisions based on generalized multichannel quantum defect theory. This approach leads to much insight into photodissociation dynamics and suggest various limiting approximations which need further testing, such as recoil or frame transformation approximations for product alignment or fine structure branching. We will also continue to develop the nonadiabatic theory of atomic line broadening in two areas. First, we will study the Lorentzian asymmetry of the core profile. Second, we will incorporate the effect of strong laser fields, including the effect of collisions in broadening the Mollow line shapes and the effect of AC Stark shifts in modifying inelastic collision cross sections.

5. PUBLICATIONS

(a) Publications of Past Year

- Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation of Molecules on Surfaces: Hydroxyl Groups on Silica Surfaces," *J. Vac. Soc. Tech.* A3, 1655 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Temperature Dependence of the Vibrational Population Lifetime of OH($v=1$) in Fused Silica," *Chem. Phys. Letters*, 117, 185 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Deactivation of Surface OH Chemisorbed on SiO₂: Solvent Effects," *J. Chem. Phys.* 82, 5216 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," *SPIE Proceedings* 533, 15 (1985).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Picosecond Vibrational Energy Relaxation of Surface Hydroxyl Groups on Colloidal Silica," *J. Chem. Phys.* 81, 2856 (1984).
- Hougen, J. T. and Ohashi, N., "Group Theoretical Treatment of the Planar Internal Rotation Problem in (HF)₂," *J. Mol. Spectrosc.* 109, 134-165 (1985).
- Hougen, J. T., "Summary of Group Theoretical Results for Microwave and Infrared Studies of H₂O₂," *Can. J. Phys.* 62, 1392-1402 (1984).
- Jacox, M. E., "Ground-State Vibrational Energy Levels of Polyatomic Transient Molecules," *J. Phys. Chem. Ref. Data* 13, 945-1068 (1984).
- Jacox, M. E., "Spectroscopy and Photochemistry of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," *Rev. Chem. Intermed.* 6, 77-120 (1985).
- Julienne, P. S., "Collision Induced Radiative Transitions at Optical Frequencies," in Phenomena Induced by Intermolecular Interactions, ed., by G. Birnbaum (Plenum Press, 1985).
- King, D. S. and Stephenson, J. C., "Kinetic Energy Disposal in the Unimolecular IRMPD of Methyl Nitrite," *Chem. Phys. Letts.* 114, 461 (1985).

- King, D. S. and Stephenson, J. C., "Infrared Multiphoton Dissociation of Methyl Nitrite in a Molecular Beam; Internal States of the Nitric Oxide Fragment," J. Chem. Phys. 82, 2236 (1985).
- King, D. S., Mantell, D. A., and Cavanagh, R. R., "NO Thermally Desorbed from a Saturation Coverage on Pt(111): Internal State Distributions," J. Chem. Phys. 82, 1046 (1985).
- King, D. S., "Product State and Kinetic Energy Distributions in the Ultraviolet Photodissociation of the NO-Ar van der Waals Molecule," J. Chem. Phys. 82, 3629 (1985).
- King, D. S. and Stephenson, J. C., "Energy Distribution in the Nitric Oxide Fragments from the ν_7 Vibrational Predissociation of NO-C₂H₄," J. Chem. Phys. 82, 5286 (1985).
- Krauss, M. and Stevens, W. J., "Electronic Structure of FeO and RuO," J. Chem. Phys. 82, 5584 (1985).
- Lovas, F. J., "Microwave Spectra of Molecules of Astrophysical Interest XXII. Sulfur Dioxide (SO₂)," J. Phys. Chem. Ref. Data 14, 395-488 (1985).
- Lovas, F. J., "Microwave Spectra of Atmospheric Species," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IIIA14.
- Lovas, F. J., "Critically Evaluated Microwave Spectral Data," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IV21.
- Maki, A. G., "Infrared Spectra and Atmospheric Chemistry," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IIIB1.
- Maki, A. G., Pine, A. S., and Dang-Nhu, M., "A Doppler-Limited Study of the Infrared Spectrum of Allene from 2965 to 3114 cm⁻¹," J. Mol. Spectrosc. 112, 459-481 (1985).
- Maki, A. G. and Wells, J. S., "High Resolution Spectrum of the ν_5 Band of Nitric Acid (HNO₃) Near 880 cm⁻¹," J. Mol. Spectrosc. 108, 17-30 (1984).
- Mies, F. H., "Adiabatic Analysis of Distant Perturbations: Application to Herzberg-Teller Vibronic Coupling Theory," Molec. Phys. 54, 1423-1436 (1985).
- Mies, F. H. and Julienne, P. S., "A Molecular Half Collision Analysis of Atomic Lineshapes in Spectral Lineshapes," Vol. 3, (ed., F. Rostas) W. de Gruyter and Co., Berlin, pp. 393-420 (1985).
- Miller, K. J., Taylor, E. R., Basch, H., Krauss, M., and Stevens, W. J., "A Theoretical Model for the Binding of cis-Pt(NH₃)₂²⁺ to DNA," J. Biomol. Struct. Dynam. 2, 1157 (1985).

- Ohashi, N. and Hougen, J. T., "The Torsional-Wagging Tunneling Problem and the Torsional-Wagging-Rotational Problem in Hydrazine," J. Mol. Spectrosc. 112, 384-400 (1985).
- Petersen, F. R., Wells, J. S., Jennings, D. A., and Maki, A. G., "Improved Deuterium Bromide 1-0 Band Molecular Constants from Heterodyne Frequency Measurements," J. Mol. Spectrosc. 107, 48-61 (1984).
- Pine, A. S., Fried, A., and Elkins, J. W., "Spectral Intensities in the Fundamental Bands of HF and HCl," J. Mol. Spectrosc. 109, 30-45 (1985).
- Pine, A. S., Lafferty, W. J., and Howard, B. J., "Vibrational Predissociation, Tunneling and Rotational Saturation in the HF and DF Dimers," J. Chem. Phys. 81, 2939-2950 (1984).
- Pine, A. S., "Tunable Laser Spectroscopy of Upper Atmospheric Molecules," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. III B8.
- Pollock, C. P., Petersen, F. R., Jennings, D. E., Wells, J. S., and Maki, A. G., "Absolute Frequency Measurements of the 00^o2-00^o0, 20^o1-00^o0 Bands of N₂O by Heterodyne Spectroscopy," J. Mol. Spectrosc. 107, 62-71 (1984).
- Raab, M. and Weber, A., "Amplitude Modulated Heterodyne Polarization Spectroscopy," J. Opt. Soc. Am. B2, 1476 (1985).
- Ratcliff, L., Konowalow, D. D., and Stevens, W. J., "Transition Moments for Low-Lying Excited States in NaK," J. Mol. Spectrosc. 110, 242 (1985).
- Rumble, J. R., Jr., Stevens, W. J., and Truhlar, D. G., "Effective Electron Correlation in the Target Wavefunction on Electron-Molecule Scattering," J. Phys. B17, 315 (1984).
- Snyder, L. E., Henkel, C., Hollis, J. M., and Lovas, F. J., "Observations of the SiO₂ Radical Toward IRC + 10216 at 1.27 Centimeters," Astrophys. J. (Letters) 290, L29-L33 (1985).
- Stevens, W. J., Basch, H., and Krauss, M., "Compact Effective Core Potentials and Efficient Shared-Exponent Basis Sets for the First- and Second-Row Atoms, Li-Ar," J. Chem. Phys. 81, 6026 (1984).
- Suenram, R. D., Lovas, F. J., and Stevens, W. J., "Reaction Products from a Microwave Discharge of N₂ and H₂S, The Microwave Spectrum Two Conformers of Sulfur Diimide (H-N=S=N-H)," J. Mol. Spectrosc. (1985).
- Weber, A., "Proceedings of the CMA/NBS Workshop on Atmospheric Spectra," November 3-4, 1983, (June 1985).
- Wells, J. S., Jennings, D. A., Hinz, A., Murray, J. S., and Maki, A. G., "Heterodyne Frequency Measurements on N₂O at 5.3 and 9.0 μ m," J. Opt. Soc. Am. B2, 857-861 (1985).

(b) Publications in Progress

- Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Electronic and Geometric Structures of $\text{Pt}(\text{NH}_3)_2^{2+}$, $\text{Pt}(\text{NH}_2)_3\text{Cl}_2$, $\text{Pt}(\text{NH}_3)_3\text{X}$ and $\text{Pt}(\text{NH}_3)_2\text{XY}$ ($\text{X}, \text{Y} = \text{H}_2\text{O}, \text{OH}$)," *J. Inorg. Chem.* (in press).
- Basch, H., Krauss, M., and Stevens, W. J., "Cation Binding Effect on H-Bonding," *J. Am. Chem. Soc.* (submitted).
- Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Binding of $\text{Pt}(\text{NH}_3)_3^{2+}$ to Nucleic Acid Bases," *J. Inorg. Chem.* (submitted).
- Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Electronic and Geometric Structures of $\text{Pt}(\text{NH}_3)_2^{2+}$, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, $\text{Pt}(\text{NH}_3)_3\text{X}$, $\text{Pt}(\text{NH}_3)_2\text{XY}$ ($\text{X}, \text{Y} = \text{OH}^-, \text{H}_2\text{O}$)," *Inorg. Chem.* (submitted).
- Basch, H., Krauss, M., and Stevens, W. J., "Cation Binding Effect on H-Bonding," *J. Am. Soc.* (submitted).
- Bodaness, R. S., Heller, D. F., Krasinski, J., and King, D. S., "Direct Two-Photon Excitation of the Tumor Localizing Photo-Sensitizer Hematoporphyrin Derivative at 750 nm via the Soret Band System," *J. Biological and Biochemical Sciences* (WERB review).
- Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of $\text{OH}(\nu=1)$ Vibrational Relaxation on SiO_2 Surfaces: Isotope and Temperature Dependence," *Phys. Rev. Lett.* (submitted).
- Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation at Surfaces," *J. Electronic Spectry.* (accepted).
- Dang-Nhu, M. and Pine, A. S., "Intensities des Raies d'Absorption dans la Bande Chaude $\nu_8 + \nu_{11} - \nu_{11}$ de l'Allene," *Can. J. Phys.* (in press).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Decay of Surface Adsorbates," *Proceedings of the 1985 Conference on Time-Resolved Vibrational Spectroscopy*, Springer-Verlag (in press).
- Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Time-Resolved Vibrational Energy Relaxation of Surface Adsorbates," *J. Vac. Sci. Tech. B*, (in press).
- Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," *J. Mol. Spectrosc.* (accepted).
- Howard, B. J. and Pine, A. S., "Rotational Predissociation and Libration in the Infrared Spectrum of Ar-HCl," *Chem. Phys. Letters* (submitted).

- Jacox, M. E., "Comparison of the Ground-State Vibrational Fundamentals of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," J. Mol. Spectrosc. 113, (in press).
- Jacox, M. E., "Reaction of F Atoms with Methyl Halides. Vibrational Spectra of CH_3XF and of $\text{H}_2\text{CX}\cdots\text{HF}$ Trapped in Solid Argon," J. Chem. Phys. 83, (in press).
- Jasien, P. G. and Stevens, W. J., "Calculated Proton Affinities for Some Molecules Containing Group VI Atoms," J. Chem. Phys. (in press).
- Jennings, D. E., Weber, A., and Brault, J. W., "Raman Spectroscopy of Gases with a Fourier Transform Spectrometer: The Spectrum of D_2 ," Appl. Opt. (submitted).
- Karpas, Z., Stevens, W. J., Buckley, T. J., and Metz, R., "The Proton Affinity and Gas Phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate, and Methyl Thiocyanate," J. Phys. Chem. (in press).
- King, D. S. and Cavanagh, R. R., "Laser Studies of Molecule-Surface Interactions," Review prepared for Springer Series in Chemical Physics (submitted).
- Krauss, M., Stevens, W. J., and Basch, H., "Relativistic Effective Potential SCF Calculations of AgH and AuH ," J. Comp. Chem. (in press).
- Lovas, F. J., "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions," J. Phys. Chem. Ref. Data (submitted).
- Mantell, D. A., Cavanagh, R. R., and King, D. S., "Internal States Distributions of NO Thermally Desorbed from Pt(111): Dependence on Coverage and Co-adsorbed CO," J. Chem. Phys. (submitted).
- Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Study of the Collisionless Photodissociation of Dimethylnitramine at 266 nm," Chem. Phys. Lett. (submitted).
- Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Induced Fluorescence Study of the Collisionless Photodissociation of Nitrocompounds at 266 nm" Chem. Phys. (in WERB review).
- Mies, F. H., Julienne, P. S., Band, Y. B., and Singer, S., "A Convergent Analysis of Radiative Matrix Elements in Atomic Lineshape Theory," J. Phys. B (submitted).
- Miller, K. J., Taylor, E. R., Basch, H., Krauss, M., and Stevens, W. J., "A Theoretical Model for the Binding of $\text{Cis-Pt}(\text{NH}_3)_2^{2+}$ to DNA," J. Biomol. Str. Dyns. (in press).
- Ohashi, N., Lafferty, W. J., and Olson, W. B., "Fourier Transform Far Infrared Spectrum of Hydrazine," J. Mol. Spectrosc. (submitted).
- Pine, A. S., Maki, A. G., and Chou, N.-Y., "Pressure Broadening, Lineshapes, and Intensity Measurements in the $2+0$ Band of NO," J. Mol. Spectrosc. (in press).

- Pine, A. S. and Fried, A., "Self Broadening in the Fundamental Bands of HF and HCl," J. Mol. Spectrosc. (in press).
- Pine, A. S. and Howard, B. J., "Hydrogen-Bond Energies of the HF and HCl Dimers from Absolute Infrared Intensities," J. Chem. Phys. (submitted).
- Rosenkrantz, M. E. and Krauss, M., "Damped Dispersion Interaction Energies for He-H₂, Ne-H₂, and Ar-H₂," Phys. Rev. (submitted).
- Suenram, R. D., Lovas, F. J., and Pickett, H. M., "Millimeter Wave Spectrum of Peroxynitric Acid," J. Mol. Spectrosc. (submitted).
- Thompson, G. A., Maki, A. G., and Weber, A., "The Infrared Spectrum of GeO," J. Mol. Spectrosc. (submitted).
- Vahala, L., Julienne, P. S., and Havey, M. D., "Nonadiabatic Theory of Fine-Structure Branching Cross Sections for NaHe, NaNe, and NaAr," Phys. Rev. A (submitted).
- Wells, J., Hinz, A., and Maki, A. G., "Heterodyne Frequency Measurements on N₂O Between 1257 cm⁻¹ and 1340 cm⁻¹," J. Mol. Spectrosc. (in press).

6. TALKS

- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Molecules on Surfaces," 31st National Meeting of the American Vacuum Society, Reno, NV, December 1984.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Gordon Conference on Dynamics of Gas-Surface Interactions, New London, NH, July 1985.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Exxon Research and Engineering Co., Annandale, NJ, May 1985.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," IBM Watson Research Center, Yorktown Heights, NY, June 1985.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," General Motors Research Labs, Warren, MI, May 1985.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Sandia National Laboratory, Livermore, CA, May 1985.
- Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Aerospace Corporation, Los Angeles, CA, May 1985.
- Casassa, M. P., "Dynamics of Vibrational Energy in Molecules: Vibrational Relaxation of Molecules Chemisorbed on Surfaces," Sandia National Laboratory, Albuquerque, NM, March 1985.
- Casassa, M. P., "Picosecond Measurements of Vibrational Relaxation on Surfaces," Surface Science Division, National Bureau of Standards, Gaithersburg, MD, February 1985.
- Casassa, M. P., Heilweil, E. J., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," Symposium on Surface Bonds, ACS National Meeting, Chicago, IL, September 1985.
- Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Microphysics of Adsorbates Conference, Santa Fe, NM, February 1985.
- Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Sandia National Labs, February 1985.
- Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Howard University, April 1985.
- Heilweil, E. J., "Vibrational Energy Decay of Surface Adsorbates," Virginia Commonwealth University, April 1985.

- Heilweil, E. J., "Vibrational Energy Decay of Surface Adsorbates," Time-Resolved Vibrational Spectroscopy Conference, Bayreuth, West Germany, June 1985.
- Heilweil, E. J., "Picosecond Vibrational Relaxation of Adsorbates at Colloidal Interfaces," Gordon Research Conference, Chemistry at Interfaces, July 1985.
- Hougen, J. T., "Point-Groups, Permutation-Inversion Groups and Extended Groups," IMS Colloquium, Okazaki, Japan, November 1984.
- Hougen, J. T., "The Philosophy and Mathematics of Constructing Effective Hamiltonians for Molecules with Large Amplitude Vibrational Motions," Seminar for the Theoretical Group at IMS, Okazaki, Japan, November 1984.
- Hougen, J. T., "Selected Topics from Atomic and Molecular Spectroscopy," IMS, Okazaki, Japan, November 1984.
- Hougen, J. T., "The Avoided Crossing Technique of Meerts and Ozier: Its Application to A values and Barrier Heights, and One Selection Rule Puzzle," Seminar for the High Resolution Group at IMS, Okazaki, Japan, December 1984.
- Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems," Seminar for High Resolution Group at IMS, Okazaki, Japan, December 1984.
- Hougen, J. T., "Application of Vibration-Rotation Tunneling Theory to the Gas Phase Water Dimer Spectrum," Molecular Spectroscopy Division Seminar, NBS, January 1985.
- Hougen, J. T., "Tunneling Motion in the Water Dimer," Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA, April 1985.
- Hougen, J. T., Four lectures on "Group Theory in Molecular Spectroscopy," at the Chemistry Department, University of California, Berkeley, CA, April 1985.
- Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," Washington Meeting of the American Physical Society, Washington, D.C., April 1985.
- Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Hougen, J. T. and Ohashi, N., "The Torsional-Wagging Tunneling Problem and Torsional-Wagging-Rotational Problem in Hydrazine," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Hougen, J. T., "The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric Top Internal Rotor Molecules Like $\text{H}_3\text{C-SiH}_3$," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

- Hougen, J. T., "Symmetry Beyond Point Groups in Molecular Spectroscopy," Department of Chemistry, University of Chicago, Chicago, IL, July 1985.
- Hougen, J. T., "Symmetry Beyond Point Groups in Molecular Spectroscopy," Seventeenth International Symposium on Free Radicals, Granby, CO, August 1985.
- Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, As Applied to the Water Dimer," American Chemical Society, Chicago, IL, September 1985.
- Hougen, J. T., "The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric-Top High-Barrier Internal Rotor Molecules," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.
- Howard, B. J. and Pine, A. S., "Near-Infrared Spectra of Rare-Gas-HCl Complexes," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Jacox, M. E., "Spectroscopic Studies of the Early Stages in the Decomposition of Energetic Materials," Workshop on the Initiation of the Chemical Decomposition of Energetic Materials, Office of Naval Research, Annapolis, MD, October 1984.
- Jacox, M. E., "Spectroscopy of Intermediates in the Decomposition of Energetic Materials. Experimental Studies at the National Bureau of Standards," Workshop on Diagnostics for Ignition Mechanisms, Army Research Office, Aberdeen, MD, November 1984.
- Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Substituted Methanes," 7th Winter Fluorine Conference, Division of Fluorine Chemistry, American Chemical Society, Orlando, FL, February 1985.
- Jacox, M. E., "Dolphus E. Milligan - A Scientific Retrospective," Dedication Symposium, Dolphus E. Milligan Science Research Institute, Atlanta University Center, Atlanta, GA, March 1985.
- Jacox, M. E., "Matrix Isolation Studies of the Decomposition and Ionization of Small Molecules at Energies Between 11.5 and 16.8 eV," Symposium on Ultraviolet Photochemistry, 68th Canadian Chemical Conference, Kingston, Ontario, Canada, June 1985.
- Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Methyl Halides," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Substituted Methanes," 5th International Colloquium on the Spectroscopy of Matrix Isolated Species, Fontevraud, France, July 1985.

- Jacox, M. E., "The Vibrational Spectrum of the COOH Free Radical Trapped in Solid Argon," 17th International Symposium on Free Radicals, Granby, CO, August 1985.
- Jacox, M. E., "Vibrational and Electronic Spectra of Transient Species Trapped in Solid Argon and Neon," Symposium on Theoretical and Experimental Studies of Transient Species, 190th National Meeting of the American Chemical Society, Chicago, IL, September 1985.
- Jasien, P. G. and Stevens, W. J., "Proton Affinities of Some Molecules Containing Group VI Atoms," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Jennings, D. E., Weber, A., and Brault, J. W., "Fourier Transform Raman Spectroscopy of H₂ and D₂ in Flames," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Julienne, P. S., "Theory of Atomic Collisions in Laser Fields," Physics Department Seminar, University of Missouri, Rolla, MO, October 1984.
- Julienne, P. S., "Nonadiabatic Half-Collision Theory of Line Broadening, Laser-induced Collisions, and Photodissociation," Atomic and Molecular Theory Group Seminar, Lawrence Livermore Laboratory, Livermore, CA, December 1984.
- Julienne, P. S., "Analytic Multichannel Theory of Molecular Dissociation," International Conference on the Physics of Electronic and Atomic Collisions, Stanford University, Palo Alto, CA, August 1985.
- King, D. S., "State Selective Studies of Molecular-Surface Dynamics," Optical Society of America National Meeting, San Diego, CA, October 1984.
- King, D. S., "State Selective Studies of Molecule-Surface Interactions," University of California, Irvine, CA, November 1984.
- King, D. S., "Dynamics in Chemical Bond Breaking Processes," Molecular Spectroscopy Division Seminar, NBS, February 1985.
- King, D. S., "Energy Distributions in Thermally Desorbed Molecules," Conference on the Dynamics of Molecular Collisions, Utah, July 1985.
- Krauss, M., "Electronic Structure of Metal Oxides," IBM, Kingston, NY, February 1985.
- Krauss, M., "Effective Potentials in Quantum Chemistry," Rensselaer Polytechnical Institute, NY, April 1985.
- Lafferty, W. J. and Olson, W. B., "High Resolution Spectrum of the ν_2 and ν_3 Bands of HOCl," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Lovas, F. J. and Suenram, R. D., "Pulsed Beam Microwave Study of the van der Waals Complex Ar...CH₂CHCN," Spring Meeting of the American Physical Society, Crystal City, MD, April 1985.

- Lovas, F. J., "Rotational Studies of Weakly-Bound Molecules by Conventional and Fourier Transform Microwave Spectroscopy," Institut für Physikalische Chemie der Universität Kiel, Kiel, Germany, September 1985.
- Lovas, F. J. and Suenram, R. D., "Pulsed Beam Microwave Study of the van der Waals Complexes Ar...CH₂CHCN and Kr...OCS," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.
- Lovejoy, R. W., Schaeffer, R. D., and Olson, W. B., "High Resolution Infrared Spectrum on SiH₃D," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Maki, A. G., "Laboratory Studies of Atmospheric Molecules at NBS," Workshop on the Spectroscopic Studies of Atmospheric Species, NASA-Langley Research Center, Hampton, VA, October 1984.
- Maki, A. G., Pine, A. S., Wells, J. S., Jennings, D. A., Fayt, A., and Goldman, A., "Laboratory Studies of the Infrared Spectra of Atmospheric Species," Topical Meeting on Optical Remote Sensing of the Atmospheric, Incline Village, Nevada, January 1985.
- Maki, A. G. and Pine, A. S., "Pressure Broadening and Intensity Measurements for the 2-0 Band of NO," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Mies, F. H., "Collisional Redistribution of Resonant Radiation in Intense Laser Fields," Conference on Dynamics of Molecular Collisions, Snowbird, Utah, July 1985.
- Ohashi, N., Lafferty, W. J., and Olson, W. B., "Far-Infrared Spectrum of the Torsional Band of Hydrazine," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Pine, A. S., "Difference-Frequency Laser Spectroscopy of Hydrogen-Bonded and van der Waals Complexes," Joint MIT-Harvard Physical Chemistry Colloquium, Harvard University, Cambridge, MA, December 1984.
- Pine, A. S., "High-Resolution Studies of Predissociation in Hydrogen-Bonded and van der Waals Complexes," Chemistry Department, University of California, Berkeley, CA, January 1985.
- Pine, A. S., "Infrared Spectroscopy of Hydrogen-Bonded and van der Waals Complexes Using a Difference-Frequency Laser," Western Spectroscopy Association Meeting, Asilomar, CA, February 1985.
- Pine, A. S., "Difference-Frequency Laser Spectroscopy of Hydrogen-Bonded and van der Waals Complexes," American Physical Society Spring Meeting, Washington, D.C., April 1985.
- Pine, A. S. and Fried, A., "Intensities and Self-Broadenings in HF and HCl," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Stevens, W. J., "Compact Effective Potentials and Basis Sets," IBM Laboratories, Kingston, NY, October 1984.

- Stevens, W. J., "Cation Binding Effect on Inidizole Tautomerism," 5th International Congress on Quantum Chemistry, Montreal, Canada, August 1985.
- Suenram, R. D. and Lovas, F. J., "Microwave Spectrum of the Ar···Acrylonitrile van der Waals Complex" 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Stephenson, J. C., "Vibrational Energy Transfer," Chemistry Department, Howard University, April 1985.
- Stephenson, J. C., "Vibrational Energy Transfer in Adsorbates on Surfaces," Chemistry Department, MIT, May 1985.
- Stephenson, J. C., "Vibrational Energy Transfer in Adsorbates on Surfaces," Gordon Conference on Molecular Energy Transfer, July 1985.
- Stephenson, J. C., "Vibrational Relaxation of Chemical Bonds in Liquids and on Surfaces," International Conference on Photochemistry, June 1985.
- Thompson, G. A., Maki, A. G., and Weber, A., "More Diode Laser Spectra of Diatomic Molecules," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Thompson, G. A., Maki, A. G., and Weber, A., "Infrared Measurements of High Temperature Diatomic Species," XVII European Congress on Molecular Spectroscopy, Madrid, Spain, September 1985.
- Weber, A., Lafferty, W. J., and Olson, W. B., "High Resolution Infrared Spectrum of Cyanogen," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.
- Weber, A., Jennings, D. E., and Brault, J. W., "Fourier Transform Raman Spectroscopy of Gases," XVII European Congress on Molecular Spectroscopy, Madrid, Spain, September 1985.
- Weber, A., Jennings, D. E., and Brault, J. W., "Fourier Transform Raman Spectroscopy of Gases," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.
- Weber, A., "Recent Work in High Resolution Molecular Spectroscopy at NBS," Physics Department, University of Bayreuth, Bayreuth, Germany, September 1985.

7. MOLECULAR SPECTROSCOPY DIVISION SEMINARS

- Allen, L. C., Department of Chemistry, Princeton University, Princeton, NJ, "Electronic Mechanism of Carbonic Anhydrase," March 1985.
- Andrews, L., Department of Chemistry, University of Virginia, Charlottesville, VA, "High and Low Energy Species: Spectroscopy of Molecular Ions and HF Complexes in Solid Argon," November 1984.
- Band, Y. B., Ben-Gurion University, Israel, "Optical Properties of Molecules with Large Excited State Absorption," July 1985.
- Band, Y. B., Ben-Gurion University, Israel, "Photodissociation of Diatomic Molecules to Atoms with Non-vanishing Angular Momentum," July 1985.
- Bowen, K. H., Department of Chemistry, Johns Hopkins University, Baltimore, MD, "Negative Ion Photoelectron Spectroscopy of Negative Cluster Ions," May 1985.
- Evenson, K., Time and Frequency Division, NBS, Boulder, CO, "Tunable Far Infrared Spectroscopy," November 1984.
- Fraser, G. T., Chemistry Department, Harvard University, MA, "Nonrigidity and Vibrational Predissociation in Ammonia van der Waals Complexes," March 1985.
- Herman, R., Physics Department, Penn State University, "Collisional Interference in the Vibration-Rotation Spectra of H₂ and HD," October 1984.
- Hirota, E., Institute for Molecular Science, Myodaiji, Okazaki, Japan, "Infrared Laser Kinetic Spectroscopy," April 1985.
- Hochstrasser, R. M., Department of Chemistry, University of Pennsylvania, PA, "Ultrafast Relaxation Processes in Condensed-Phase Molecular Systems," May 1985.
- Howard, B. J., Physical Chemistry Laboratory, Oxford University, England, "IR Studies on Intermolecular Interactions in Weakly Bound Species," April 1985.
- Jackson, W. M., Chemistry Department, Howard University, "Laser Studies of Reaction Dynamics in Gases and on Surfaces," September 1985.
- Kunz, T., Department of Chemistry, Rice University, Houston, TX, "Photochemistry of Formyl Fluoride," February 1985.

- Ladik, J., University Erlangen-Nürnberg, Germany, "Quantum Theory of Polymers: Solid State Aspects," September 1985.
- Mills, I. M., University of Reading, England, "Molecular Vibrations Seen as Local Modes," April 1985.
- Moore, R., Department of Chemistry Virginia Commonwealth University, VA, "Picosecond Intermolecular Vibrational Relaxation in the Gas Phase," January 1985.
- Pickett, H. M., Jet Propulsion Laboratory, Pasadena, CA, "Spectroscopy in the World Above One Terahertz," March 1985.
- Schweitzer, E., Chemistry Department, MIT, Cambridge, MA, "Spectroscopic Probes of Infrared Multiphoton Dissociation," February 1985.
- Shostak, S., University of Rochester, Rochester, NY, "Studies of Infrared Laser Excited Molecules by MBER and Maser Spectroscopy," February 1985.
- van Duijnen, P., Theoretical Chemistry Group, Laboratory of Chemical Physics, Cromingen, The Netherlands, "Reaction Field Hamiltonians and Applications to Biomolecules," June 1985.

8. TECHNICAL AND PROFESSIONAL COMMITTEE
PARTICIPATION AND LEADERSHIP

Hougen, J. T.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

Member of the subcommittee on Notations and Conventions for Molecular Spectroscopy for the "IUPAC" Commission on Molecular Structure and Spectroscopy."

Jacox, M. E.

Member, Editorial Advisory Board, Reviews of Chemical Intermediates.

Member of a National Science Foundation panel for the review of proposals for Engineering Research Equipment Grants and Research Initiation Grants.

Member, Admissions Committee, NBS Chapter, Sigma XI.

King, D. S.

Member, DOE University Research Instrumentation Grant Award Review Panel.

Lovas, F. J.

Member, International Astronomical Union
Commission 14: Fundamental Spectroscopic Data.

Maki, A. G.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

Weber, A.

Editorial Advisory Board, Journal of Raman Spectroscopy.

Member, Program Committee, 10th International Conference on Raman Spectroscopy, 1986.

Chairman, Williams-Wright Awards Committee, Coblenz Society.

Director and Chairman, Organizing Committee, NATO Advanced Research Workshop on "Structure and Dynamics of Weakly Bound Molecular Complexes."

9. PROFESSIONAL INTERACTIONS, CONSULTING
AND ADVISORY SERVICES

Casassa, M. P.

Dr. R. R. Cavanagh, Surface Science Division, on picosecond infrared laser studies of vibrational relaxation of adsorbed molecules.

Dr. K. C. Janda, California Institute of Technology, on studies of the infrared photodissociation of van der Waals molecules.

Heilweil, E. J.

Professor R. M. Hochstrasser, University of Pennsylvania, on transient grating phenomena in molecular solutions.

Professor G. Ritchie, Department of Physics, Rider College, on dielectric perturbations of surface plasmon dynamics.

Dr. C. Sandhoff, AT & T Bell Communications, on pressure dependent lifetimes of colloidal semiconductor excited states.

Hougen, J. T.

Distinguished Visiting Foreign Professor, IMS, Okazaki, July-December 1984.

Professor R. Saykally and students, University of California, Berkeley, on spectra of floppy molecular ions.

Professor T. Oka and students, University of Chicago, on spectra of floppy molecular ions.

Jacox, M. E.

Professor R. F. Curl, Department of Chemistry, Rice University, on the infrared spectrum of HC_2 .

Professor L. Andrews, Department of Chemistry, University of Virginia, on the infrared spectra of partially deuterated ethylenes.

Dr. Victor Maroni, Argonne National Laboratory, on the infrared spectrum of FON.

Professor E. K. C. Lee, Department of Chemistry, University of California, Irvine, on the spectrum of matrix-isolated H_2S .

Professor P. Thaddeus, Goddard Institute for Space Studies and Physics Department, Columbia University, on the spectrum of C_3H_2 .

Professor Douglas D. Davis, Department of Chemistry, Georgia Institute of Technology, on the spectra of matrix-isolated nitrogen oxides.

Julienne, P. S.

Dr. M. Havey, Old Dominion University, on interpretation of radiative redistribution experiments.

Dr. J. Weiner, University of Maryland, on interpretation of Na₂ photodissociation experiments.

Dr. S. Singer, University of Pennsylvania, on development of a close coupled photodissociation code.

Dr. Y. B. Band, Ben-Gurion University, on calculating atomic line broadening matrix elements.

King, D. S.

Dr. R. Bodanness, NIH, on the role of biphotonic processes in the photo-activated generation of singlet oxygen.

Dr. R. R. Cavanagh and Dr. W. Gadzuk, on experimental and theoretical aspects of molecular dynamics of the gas-surface interface.

Krauss, M.

Dr. E. C. Clementi and Dr. M. Dupuis, IBM, Kingston, NY, on biochemical molecules.

Dr. K. J. Miller, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, on Pt amine drug interactions with DNA.

Lafferty, W. J.

Dr. J. P. Sattler, Harry Diamond Laboratory, consulting on optically pumped far infrared laser line assignments.

Lovas, F. J.

National Science Foundation, member of the Physics and Astronomy Panel for the 1984 Graduate Fellowship Program.

Professor L. E. Snyder, University of Illinois and Dr. J. M. Hollis, NASA/Goddard Space Flight Center, collaborations and consultations on interstellar molecular searches.

Dr. R. Wattenbach and Dr. T. Wilson, Max-Planck Institute for Radioastronomie, Bonn, provided spectroscopic information on O₃ and H₂CS for atmospheric and interstellar measurements.

Maki, A. G.

Dr. A. Goldman, University of Denver, collaboration on studies of Nitric Acid spectra.

Dr. A. Fayt, Universite Catholique de Louvain, Belgium, collaboration on the analysis of the ν_2 and ν_4 bands of HNO_3 and on Lamb-dip measurements of laser-Stark spectra.

Dr. J. Kauppinen, University of Oulu, Oulu, Finland, collaboration on the measurement and analysis of spectra of OCS , CO_2 , and N_2O for use in the calibration of spectrometers and tunable laser devices.

Dr. J. Wells, Time and Frequency Division, NBS-Boulder, collaboration on the frequency measurement and analysis of N_2O and NO absorption lines using heterodyne techniques.

Dr. C. Chackerian, NASA Ames Research Center, Moffett, CA, collaboration on the use of the Herman-Wallis effect to measure the intensity of the ClO fundamental band.

Pine, A. S.

Dr. A. Fried, Gas and Particulate Science Division, NBS, collaboration on spectral line intensities and broadenings in HF and HCl .

Dr. R. M. Herman and J. P. Looney, Department of Physics, Penn State University, University Park, PA, collaboration on line broadening mechanisms in HF and HCl .

Stephenson, J. C.

Dr. J. W. Perry, Jet Propulsion Laboratory, Pasadena, CA, on picosecond studies of energy transfer in liquids.

Stevens, W. J.

Dr. M. Dupuis, Lawrence Berkeley Laboratory, on quantum chemistry calculations for large molecules.

Suenram, R. D.

Professor L. E. Snyder, University of Illinois, collaborations on radio astronomy searches for interstellar molecules.

Dr. H. M. Pickett, Jet Propulsion Laboratory, collaborations on analysis of (HOONO_2) and CH_2FOH rotational spectra.

Professor C. W. Gilles, Rensselaer Polytechnic Institute, advice on construction of pulsed Fourier transform microwave spectrometer.

Dr. G. T. Fraser, Harvard University, consultation and data on $\text{Ar} \cdots \text{NH}_3$, and $\text{NH}_3 \cdots \text{NH}_3$ van der Waals complexes.

Professor R. L. Kuczkowsky, and Dr. K. W. Hillig, II, University of Michigan, advice on construction of pulsed Fourier transform microwave spectrometer.

Professor S. G. Kukolich, University of Arizona, advice on construction of pulsed Fourier transform microwave spectrometer.

Professor S. Ross, University of Alberta, data fitting for $\text{H}_2\text{CO} \cdots \text{HF}$ hydrogen bonded species.

Weber, A.

Professor L. Henry, University de Paris, collaborative research on the Fourier transform spectroscopy of metal clusters.

Dr. J. W. Brault, National Solar Observatory, Tucson, AZ, collaboration on Raman Spectroscopy of gases with Fourier transform techniques.

Dr. K. Narahari Rao, Ohio State University, Columbus, OH, discussions on the organization of the 1985 Columbus Symposium.

Drs. A. Harvey, Naval Research Laboratory, I. W. Levin, National Institute of Health, Dr. G. Rosasco, Temperature and Pressure Division, NBS, and Dr. J. Nibler, Chemistry Department, Oregon State University, discussions on the planning for the 10th International Conference on Raman Spectroscopy, 1986.

10. VISITING SCIENTISTS

The Molecular Spectroscopy Division has been host in the past year to the following scientists who have worked with NBS scientists on problems of mutual interest.

Adams, George, A., Ballistics Research Laboratory, works with M. Krauss on electronic structure codes for the chemistry and spectroscopy of large molecules.

Basch, Harold, Bar Ilan University, Israel, is engaged in research on metal interactions with biomolecules. He works with M. Krauss.

Bevan, John W., Chemistry Department, Texas A & M University, worked with W. J. Lafferty and W. B. Olson on the Fourier transform infrared spectra of hydrogen bonded molecules.

Bodaness, Robert S., National Institutes of Health, worked with D. S. King on laser photosensitization processes in biological samples.

Chou, N.-Y., Chemistry Department, Howard University, worked with A. S. Pine on collisional line broadening problems.

Ho, P.-T., Electrical Engineering Department, University of Maryland, worked with J. C. Stephenson on research with picosecond lasers.

Hollis, Jan Michael, NASA/Goddard Space Flight Center, works with F. Lovas and R. Suenram on software development for automated microwave spectrometer and collaborates on astronomical studies.

Howard, Brian, Oxford University, Oxford, England, worked with A. S. Pine on high resolution infrared spectroscopy of the rare gas-HCl van der Waals molecules.

Jennings, Donald E., NASA/Goddard Space Flight Center, works with A. Weber on a project to do Raman spectroscopy of gases with the Fourier transform spectrometer of the National Solar Observatory (Kitt Peak).

Konowalow, Daniel D., Professor at SUNY-Binghamton, New York, works with M. Krauss on studies of electronic structure of alkali and alkaline earth molecules.

Lengsfield, Byron H., Ballistic Research Laboratory, works with M. Krauss on electronic structure codes for the chemistry and spectroscopy of large molecules.

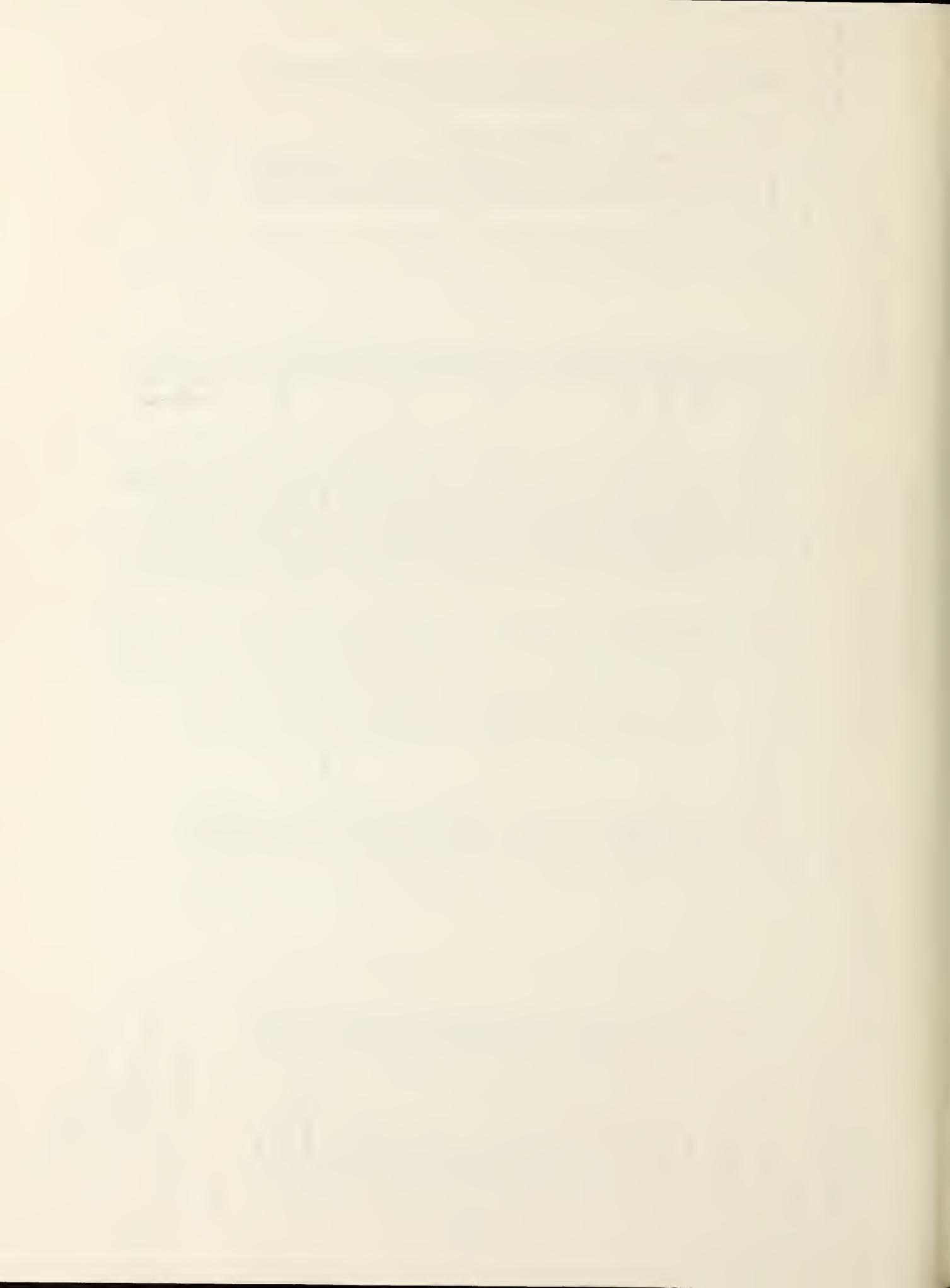
Leubner, Christoph, J., Institut für Theoretische Physik, Universität Innsbruck, Austria, worked with J. T. Hougen on improved least squares determination of potential energy surfaces from spectroscopic data.

- Lovejoy, Roland W., Chemistry Department, Lehigh University, works with B. Olson on the infrared spectrum of deuterated silanes.
- Mialocq, John-Claude, Department de Physico-Chemie, Centre d'Etudes Nucleaires de Saclay, France, worked with J. C. Stephenson on problems of vibrational relaxation, photo-dissociation, and fluorescence and absorption spectroscopy on a picosecond time scale.
- Mills, Ian M., Department of Chemistry, Reading University, Reading, England, worked with W. J. Lafferty on the spectroscopy of hydrogen bonded molecules and the theoretical relationships between normal and local mode models of molecular vibrations.
- Ohashi, Nobukimi, Kanazawa University, Physics Department, Japan, works with A. S. Pine, J. T. Hougen, W. J. Lafferty and B. Olson on high resolution infrared spectroscopy of hydrazine and of hydrogen bonded molecules.
- Sattler, Joseph P., Harry Diamond Laboratories, U. S. Army, collaborates with W. Lafferty and A. Maki on precise line frequency measurements in the infrared.
- Vahala, Linda L., Physics Department, Old Dominion University, Norfolk, VA, worked with P. S. Julienne on the theory of molecular line broadening and final state branching ratios for the resonance transitions of alkali atoms perturbed by rare gas collision partners.
- Wofford, Billy A., Chemistry Department, Texas A & M University, worked with W. J. Lafferty and W. B. Olson on the Fourier transform infrared spectra of hydrogen bonded molecules.

SURFACE SCIENCE (541) CHEMICAL KINETICS (542) CHEMICAL THERMODYNAMICS (543) MOLECULAR SPECTROSCOPY (545)

NAME	EXT.	NAME	EXT.	NAME	EXT.	NAME	EXT.
C. Powell, Chief	2161	S. Stein, Chief	2792	S. Abramowitz, Chief	2131	A. Heber, Chief	2021
or	2188	K. Randolph, Sec.	2792	P. Edgeworth, Sec.	2131	A. Flynt, Sec.	2021
L. Johnson, Sec.	2161	M. Altstein*	2439	D. Bickham##	3632	H. Basch#	2774
G. Reyna, Sec.	2161	W. Braun	2091	S. Bruce	2134/2738	R. Rodaness*	2766
D. Barak*	2784	R. Brown	2187	T. Buckley	2439/2738	M. Casassa+	2766
D. Burgess+	2743	R. Chen*	2111	M. Burns^^	2738	L. Elwell	2755
R. Cavanagh	2766	R. Cvetanovic++	2111	K. Churney	2738/2765	G. Fraser+	2719
G. Chambers*	2787	A. Fahr*	2111	D. Cockrell##	2110	E. Hellwell	2766
P. Connelly^	2756	R. Hampson	2565	J. Colbert	2134/2135	J. Hollis*	2023
W. Clinton*	2998	J. Heron	2091	H. DeVoe*	2735	J. Hougen	2021
W. Egelhoff	2788	J. Huggens	2734	D. Dilmars	2786	M. Jacox	2754
N. Erickson	2789/2769	R. Huie	2151	E. Domalski	2131	P. Jasien+	2694
J. Fine	2787	S. Kafafi*	2111	P. Fagan##	3632	D. Jennings*	2021
S. Gadzuk	2161	M. Kurylo	2080	E. Gajewski	2027	P. Julienne	2774
J. Girvin	2789	A. Laufer*	2151	D. Garvin	2773	D. King	2766
Y. Hashiguchi*	2789	R. Levin	2439	R. Goldberg	2747	D. Konowalow*	2774
T. Jach	2052	S. Lias	2439/2078	R. Harrison+	2785/3634	M. Krauss	2165
R. Kelley	2743	R. Martinez	2187	B. Haring++	3632	C. Kurtz	2023
L. King	2784	M. Mautner	2784	C. Jackson<	2110	W. Lafferty	2719
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		G. Zumwalt	2174	I. Weber*	2785		
				A. Wlodawer	2785/3634		
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				N. Young++	3632		

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This report summarizes research projects, measurement method development, testing and data evaluation activities carried out during Fiscal Year 1985 in the NBS Center for Chemical Physics. These activities fall in the areas of surface science, chemical kinetics, chemical thermodynamics and molecular spectroscopy.

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